

Advances in **ORGANOMETALLIC CHEMISTRY**

EDITED BY

F. G. A. STONE

DEPARTMENT OF INORGANIC CHEMISTRY
SCHOOL OF CHEMISTRY
THE UNIVERSITY
BRISTOL, ENGLAND

ROBERT WEST

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

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List of Contributors

Numbers in parenthesis indicate the pages on which the authors' contributions begin.

JOHN BIRMINGHAM (365), *Arapahoe Chemicals, Inc., Boulder, Colorado*

E. DE BOER (115), *Koninklijke/Shell-Laboratorium, Amsterdam, Holland*

M. L. H. GREEN (325), *Inorganic Chemistry Laboratory, University of Oxford, Oxford, England*

R. B. KING (157), *Mellon Institute, Pittsburgh, Pennsylvania*

R. KÖSTER (257), *Max-Planck Institut für Kohlenforschung, Mülheim/Ruhr, Germany*

P. L. I. NAGY* (325), *Inorganic Chemistry Laboratory, University of Oxford, Oxford, England*

G. N. SCHRAUZER (1), *Institut für Anorganische Chemie der Universität München, Munich, Germany*

H. A. SKINNER (49), *Chemistry Department, University of Manchester, Manchester, England*

* Deceased

Some Advances in the Organometallic Chemistry of Nickel

G. N. SCHRAUZER

*Institut für Anorganische Chemie der Universität München,
Munich, Germany*

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I

INTRODUCTION

After the discovery of nickel carbonyl $[\text{Ni}(\text{CO})_4]$ by Mond *et al.* (1) in 1890 nearly 50 years elapsed before the extraordinary catalytic activity of the carbonyl began to be recognized. In the period 1939–1940 Reppe (2) discovered the now famous carbonylation and cyclization reactions of acetylenes and olefins which are catalyzed by nickel carbonyl or by complexes derived therefrom. This, and his other work involving acetylene and olefin chemistry initiated further studies, in both industrial and academic laboratories. All this work played an essential part in the many recent developments in the chemistry of π complexes of transition metals. At first for nickel preparative success in the synthesis of π complexes was largely confined to cyclopentadienyls. In fact it appeared as if this transition metal did not have a pronounced tendency to form π complexes with unsaturated hydrocarbons at all. Very recently, however, the nickel atom “gave in” to the combined efforts of several research groups, and some interesting and reactive π complexes have now become known.

It is the purpose of this review to describe developments in the catalytic chemistry of nickel carbonyl, as well as the new π complexes of nickel. Related topics, such as the cyclopentadienyls, cyclobutadienyls, cyanyls, acetylides, or alkyls of nickel will not be discussed unless they are directly related to the above subject matter. Carbonylation reactions will be described first. Apart from the historical aspect, these provide several introductory examples for the various topics reviewed in the later sections.

II

CATALYTIC REACTIONS WITH NICKEL CARBONYL

A. Carbonylation of Alkynes

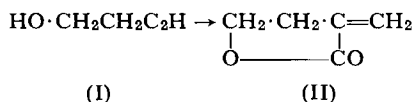
1. Reaction Conditions and Scope

In an attempt to prepare acetylenic aldehydes from acetylene, carbon monoxide, and water in the presence of nickel carbonyl and acids Reppe and co-workers (2, 3) observed formation of acrylic acid. The reaction was soon extended to substituted acetylenes and was found to be general (2, 3, 4). The term "carbonylation" was suggested for describing this group of reactions and we will use it here, although it is not generally accepted in the literature. The reaction can be performed either stoichiometrically (nickel carbonyl is the source of carbon monoxide and is used in stoichiometric quantities) or catalytically (nickel carbonyl, present in catalytic amounts, is continuously regenerated under carbon monoxide pressure). If the carbonylation is conducted in the presence of alcohols, mercaptans, amines, or organic acids, their esters, thioesters, amides, or anhydrides, are obtained respectively. The reaction was originally represented by Eq. (1)



More recent work (5), however, indicates that the actual stoichiometry is more complicated. The synthesis is preferably performed in the presence of aqueous hydrochloric, acetic, or phosphoric acids, at temperatures between 50–80° C. If anhydrous acids are used, extensive hydrogenation of the acrylic acid to propionic acid is observed (2, 3). This is attributed to hydrogenation by the hydrogen formed during reaction. Of all the metal carbonyls only cobalt carbonyl can replace nickel. Iron carbonyls do not react when used alone, but a partial conversion occurs if iron pentacarbonyl is mixed with nickel carbonyl. In the catalytic process an equimolecular mixture of acetylene and carbon monoxide is treated under pressure at 120–150° C with either nickel carbonyl or nickel, in the presence of water and an acid. Good results are also obtained using a mixture of metallic nickel and nickel iodide. Particularly well-suited, because of its ready convertibility into nickel carbonyl, is the complex $\text{NiBr}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3 \cdot 2\text{C}_4\text{H}_9\text{Br}$ (3). The carbonylation of substituted acetylenes yields unsaturated carboxylic acids. Successful carbonylations have been performed with phenylacetylene, vinylacetylene, phenylmethylacetylene, tolane (diphenyl acetylene), propargyl alcohol, butyne-1-ol-3, butyne-2-diol-1,4 and many other alkynes.

It is interesting to note that a naturally occurring antibiotic, methylene-butylolactone (II) has been synthesized by carbonylating the acetylenic carbinol (I) (6):



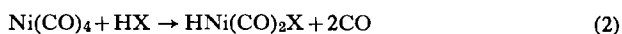
2. Mechanism

It was assumed (2, 3) as a working hypothesis, that the initial products of the carbonylation of acetylenes were cyclopropenones which, under the reaction conditions, undergo ring opening. This suggestion is invalidated by the fact that cyclopropenones are never detected among the reaction products. More recently it has been shown that diphenylcyclopropenone reacts with nickel carbonyl only after the three-membered ring ketone has been decomposed into carbon monoxide and diphenylacetylene (7). The carbonylation reaction generally requires an induction period, the length of which varies with the acetylenic reactant, the acid, and the temperature (5). The nature of the solvent is unimportant, but water is an essential reaction participant (5). In fact it appears as if free acrylic acids are formed in all cases and that the presence of, for example, an alcohol causes ester formation in a second step. In the absence of water side reactions occur, and only small amounts of unsaturated acids are isolated. Jones *et al.* (5) have also concluded that the acid molecules rather than protons participate in the main reaction.

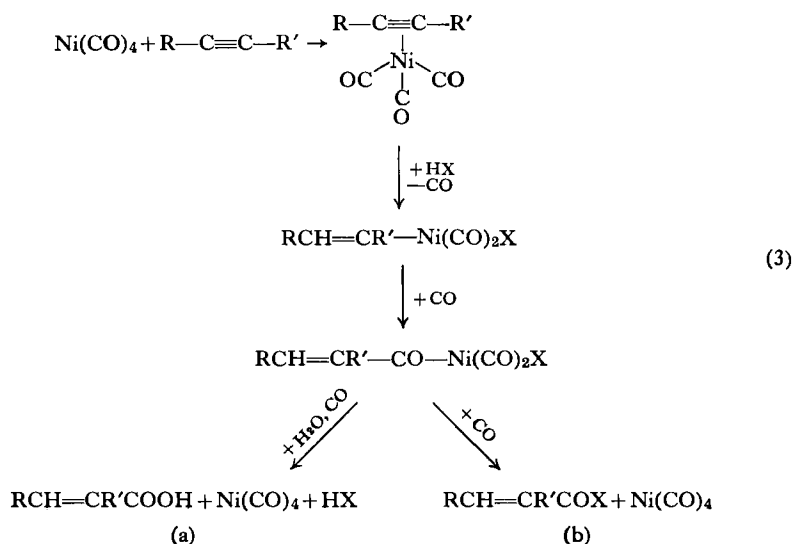
A particular acetylene can afford various products depending on the conditions. Diphenylacetylene in the presence of water, acetic acid, and alcohol, affords 38% *trans*-PhCH:C(Ph)COOH and 10% of its ethyl ester (5). Tolane can also be carbonylated in alkaline solutions (8) where a complex carbonylate, possibly $\text{Ni}_3(\text{CO})_8^{2-}$, is the source of carbon monoxide. Under these conditions tetraphenylbutadiene is isolated in addition to *trans*-PhCH=C(Ph)COOH. The carbonylation of diphenylacetylene in dioxane in the presence of absolute alcohol and concentrated hydrochloric acid affords 1,2,3,4-tetraphenyl-2-cyclopentene-1-one (9). Finally, in inert solvents diphenylacetylene reacts with nickel carbonyl, forming both tetraphenylcyclopentadienone and a π complex, bis(tetraphenylcyclopentadienone)-nickel (10) (see Section VI). Since cyclopentadienones are often formed by treating alkynes with metal carbonyls other than nickel carbonyl the carbonylation reaction with this carbonyl must be closely related. The only difference apparently arises from the presence of

water and the acid, these constituents affecting the nature of the end products by reacting with an intermediate nickel carbonyl-alkyne complex. The nature of this intermediate is still unknown and the mode of interaction with the acid molecule not yet understood.

It has been suggested (11) that during the induction period a carbonium ion is formed from the proton of the acid and the acetylene molecule, which then reacts with nickel carbonyl. However, it is rather unlikely that this should be so. Acetic acid, even under the conditions of the carbonylation reaction, definitely is not polar enough to protonate alkynes. Very recently (12) it has been suggested that during the induction period a halonickel dicarbonyl hydride is formed, according to Eq. (2)



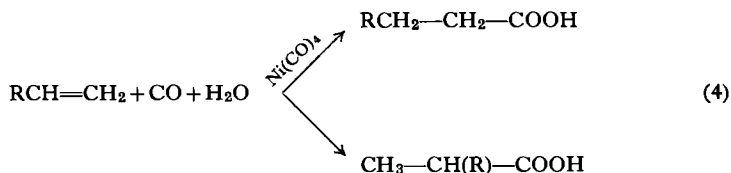
Nickel carbonyl, however, does not react with acids to form such complexes. Nevertheless, it is possible that a reaction similar to (2) could occur with an intermediate alkyne-nickel carbonyl complex, giving rise to the formation of an alkenylnickel dicarbonyl halide, $\text{RCH}=\text{CH}-\text{Ni(CO)}_2\text{X}$, which could then yield the unsaturated acid according to Eq. (3a) or (3b) (12). This reaction formally would resemble the carbonylation of allyl halides, discussed in Section II, C. Divinyl ketones may be formed as by-products of carbonylation (13), and the stereochemistry of addition to the acetylenic linkage is reported to be exclusively *cis* (13).



B. Carbonylation of Olefins

1. Reaction Conditions and Scope

Carbonylation of olefins (14) requires temperatures of 160–300° C, and can be performed stoichiometrically as well as catalytically. For the latter process total pressure of 150 to 300 atm of carbon monoxide and the olefin are required. The general reaction may be represented by Eq. (4)



Although the reaction is frequently performed in the presence of small amounts of mineral acids these are not a necessary reaction participant and the water may be replaced by alcohols, mercaptans, ammonia, amines, and organic acids. With acetylenes and alcohols the esters are formed at a distinctly slower rate than the free acids, and temperatures of 120–220° C are required. Nevertheless, yields of ester with olefins having four to eighteen carbon atoms are reported to be 90%. Various by-products are produced, e.g. carbonic acids, aldehydes, ethers, and other olefins. With ethylene small amounts of polyethylene and some higher carboxylic acids are also formed (14).

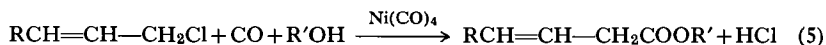
A large number of olefins have been successfully carbonylated, among them ethylene, propylene, butylene, octene, dialkylethylenes, cyclohexene, cyclooctatetraene, and styrene. Nickel carbonyl can be replaced by mixtures of $\text{Co}_2(\text{CO})_8$ with CoI_2 , NiCl_2 with Ni, or Ni with CuI. Also nickel propionate, iron pentacarbonyl, and nickel on silica may be used. Apparently, no mechanistic study of this reaction has been performed or published so far.

Alcohols and linear or cyclic aliphatic ethers can be carbonylated to mono- or dicarboxylic acids using Ni(CO)_4 in the presence of a "co-catalyst," e.g., CuI or NiI_2 (15). Reaction probably proceeds via olefinic intermediates formed by dehydration of the alcohol or ether. Thus, 1-octanol and 2-octanol both yield the same acid, 2-methyloctanoic (15a).

C. Carbonylation of Allylic Compounds

Reactions of nickel carbonyl with allylic halides have been studied by Chiusoli (16). At 100° and 50 atm of carbon monoxide in the presence of

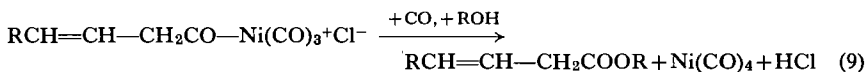
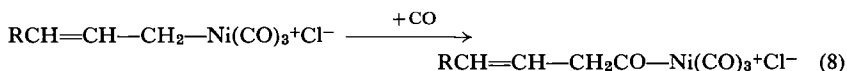
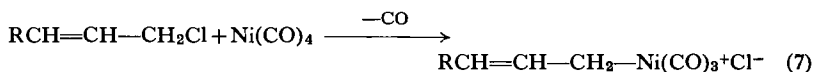
water, alcohol, and acid, an allylic chloride reacts according to Eq. (5) (16)



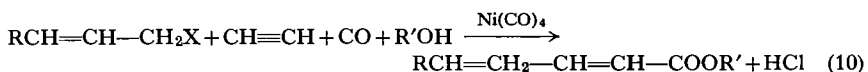
At ordinary pressure only small amounts of acid are isolated; instead, dimerization of the allyl groups occurs (16, 17) (Eq. 6)



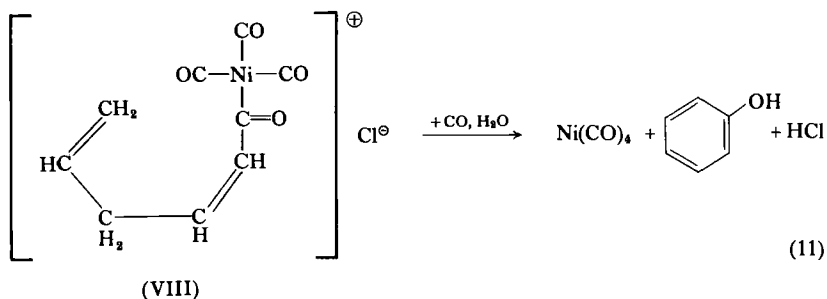
It has been proposed (16) that carbonylation proceeds according to Eqs. (7), (8), and (9)



Carbonylation of allylic halides in the presence of an acetylene occurs with insertion of one acetylene molecule, according to Eq. (10) (16)

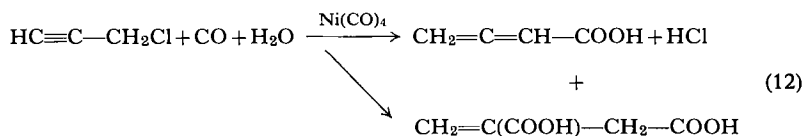


Phenol is obtained as a by-product and is probably formed in a cyclic transition state (VIII), Eq. (11)

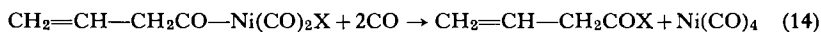
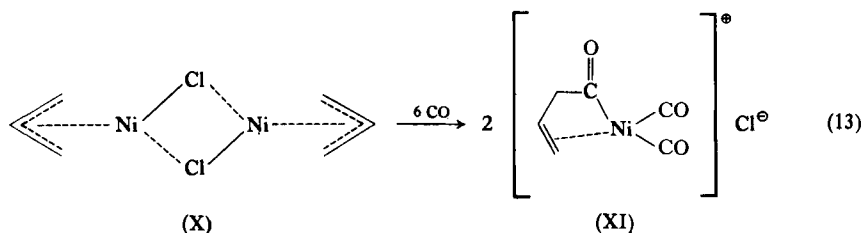


In this connection it is worth noting that phenol is also formed in 97% yield by heating hexadienoic acid ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{COOH}$)

with zinc chloride and acetic anhydride (18). Interestingly, carbonylation with propargyl chloride occurs without acetylene insertion (16)



It has recently been suggested (19) that π -allylnickel complexes are intermediates in reactions involving allylic halides. Although π -allylnickel chloride-triphenylphosphine (IX) is formed from allyl chloride and $\text{Ni(CO)}_3\text{P(C}_6\text{H}_5)_3$ without yielding a carbonylation product (20), the dimeric π -allylnickel chloride (X) [prepared (13) by heating allyl chloride with nickel carbonyl in benzene solution] reacts rapidly with carbon monoxide to form butenoylnickel dicarbonyl chloride (XI) (Eq. 13). Moreover, this complex is converted by additional carbon monoxide into butenoyl chloride and nickel carbonyl (13), Eq. (14)



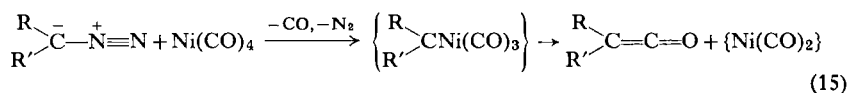
Furthermore, a mixture of acetylene and carbon monoxide reacts with π -allylnickelbromide dimer at 0°C in ether solution to give nickel carbonyl and probably hexadienoyl bromide (13). These experiments indicate that the carbon monoxide must be coordinated to the metal in order to react with the allylic system. Such a mechanism of initial coordination probably also applies to the acetylenes.

D. Miscellaneous Carbonylation Reactions

Under rather vigorous conditions aryl halides may be carbonylated in the presence of nickel carbonyl, water, or alcohol and acid, thereby yielding aryl carboxylic acids or esters, respectively (21-23).

Nickel carbonyl is also an effective dehalogenation agent. Apart from allyl halides (see above) *gem*-dihalides, e.g. dichlorodiphenylmethane, react with the carbonyl to form tetrasubstituted ethylenes (24). It is to be expected that carbonylation reactions would also occur in this case if the reaction were conducted under CO pressure.

Diazoalkanes are decomposed by nickel carbonyl yielding nitrogen and reaction products indicative of the presence of carbenes as intermediates (25). Although carbenes usually show little tendency to combine with carbon monoxide, formation of ketenes was detected by decomposing the diazoalkanes in the presence of excess nickel carbonyl. This carbonylation of carbenes undoubtedly occurs via nickel-carbene complexes (25)



Diazonium salts also readily react with nickel carbonyl, yielding mainly carboxylic acids and ketones in the presence of water and hydrochloric acid (26, 27). Iron pentacarbonyl and dicobalt octacarbonyl with diazonium salts behave similarly, but the hexacarbonyls of chromium and molybdenum are virtually ineffective. This reaction may be considered as a transition metal-catalyzed carbonylation of aryl radicals, and is closely related to the Meerwein reaction (26).

III

SUBSTITUTION REACTIONS WITH NICKEL CARBONYL

The substitution of CO in metal carbonyls by olefinic and acetylenic compounds is one of the chief methods for preparing π complexes of transition metals. Unfortunately this procedure fails almost completely when applied to nickel carbonyl, and this may be one of the reasons why until recently no π complexes of nickel with olefinic or acetylenic ligands were known. The reasons for this behavior of nickel carbonyl will become clearer, if both its electronic structure and the mechanism of the ligand exchange reactions are considered.

A. General Remarks on the Electronic Structure of Nickel Carbonyl

The Ni—C bonds in nickel carbonyl are tetrahedral and of comparable strength to those in metal alkyls (28). To stabilize the coordinative Ni—C

bonds, dative π bonding is required to remove excessive negative charge from the nickel atom. If there were no π bonding at all, the coordinative σ - and π -bonding interactions would produce five antibonding MO's mainly localized at the nickel atom which would be occupied by the ten available nickel ($3d/4s$) electrons (29). Consequently only a small net bonding energy could result. However, two of the $3d$ orbitals (mainly the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals) may overlap appreciably with the antibonding π^* orbitals of the carbon monoxide molecules and this will reduce the antibonding character of the two $3d$ orbitals (29). In view of a comparatively large energy difference between the $3d$ and the $\pi_{C=O}^*$ orbitals, dative π bonding, although necessary, will not be very effective. It will become larger if the effective Coulomb term of the central metal is lowered, e.g., by giving it a negative electronic charge, but this in turn weakens the coordinative σ and π bonds. Edgell *et al.* (30) demonstrated the change in bond character in the isoelectronic series $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$. The CO-stretching infrared frequencies decrease considerably in going from $Ni(CO)_4$ to $Fe(CO)_4^{2-}$, indicating a significant increase of dative π bonding in the given order. Thermochemical data (31) suggest that among the carbonyls of chromium, iron, and nickel, the Ni—C bonds are the weakest; approximate bond energies being 55, 58, and 46 kcal respectively, assuming valence states of d^6 , d^8 , and d^{10} for the central atoms (32, 32a).

B. Mechanism of Ligand Exchange Reactions

Ligand exchange reactions with labeled carbon monoxide performed by Basolo and Wojcicki (32) show that the carbonyls $V(CO)_6$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ exchange CO groups only slowly, whereas $Ni(CO)_4$ and $Co_2(CO)_8$ exchange rapidly. The kinetic lability of nickel carbonyl can in part be attributed to the thermodynamic weakness of the Ni—C bonds. The essential point, however, is that the exchange rate is independent of carbon monoxide concentration which supports a dissociative mechanism.



The Arrhenius activation energy for this rate-determining dissociation is 13 kcal/mole (in toluene solution). This value agrees well with the activation energy of the thermal and photochemical decomposition of nickel carbonyl in which the above dissociation (Eq. 16) is also rate determining (33, 34, 35).

The estimated average bond energy for the Ni—C bond lies in the range of 42–77 kcal and thus is much larger than the energy necessary to remove the first CO molecule. This suggests considerable π -bond stabilization of the resulting “fragment” $\text{Ni}(\text{CO})_3$ (32).

It follows from Kimball's group-theoretical considerations (36) that it is only possible to form two strong π bonds from the central atom A to the ligands B in a tetrahedral molecule AB_4 , whereas a triangular planar molecule could be stabilized by three strong π bonds. In the sp^2 $\text{Ni}(\text{CO})_3$ fragment two of these π orbitals are filled and can effectively overlap with the antibonding ligand orbitals. It was therefore concluded (32) that the driving force for the dissociative exchange mechanism may be the stabilization effect of π bonding in the transition state. Ligand exchange reactions with various phosphines were performed by Meriwether and Fiene (37) and allow similar conclusions. Evidently dissociative exchange mechanisms are general for tetrahedral complexes of zero-valent nickel. It was found that if the entering ligand L is predominantly σ bonding, the remaining Ni—C bonds in the carbonyl complex will be more strongly stabilized by π bonding. Similar effects have also been demonstrated by measurements of the stretching force constants of the CO and Ni—C bonds in homologous series of complexes $\text{Ni}(\text{CO})_{4-x}\text{L}_x$, where L is a phosphine (38).

As a consequence of enhanced π -bond stabilization of the remaining Ni—C bonds, the exchange rate for carbon monoxide and additional phosphines decreases as x in $\text{Ni}(\text{CO})_{4-x}\text{L}_x$ increases (37, 32). This explains why it is frequently observed that not all CO groups can be substituted by phosphines. A total replacement should only be possible if the ligands have comparable σ - and π -bonding abilities with carbon monoxide (e.g., the halides of phosphorus or some isonitriles). The first steps of the ligand exchange may be represented by Eqs. (16–19):



If π -bond stabilization is accepted as being the driving force for CO replacement, then one would predict that *simple* olefins should not react with nickel carbonyl to yield stable substitution products. Successful exchange

reactions are expected, however, if the olefinic ligands are strongly π bonding. A number of such ligands has been found and their reactions with nickel carbonyl will be discussed in the following sections.

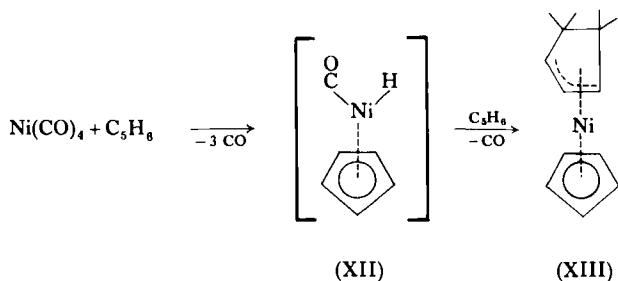
IV

REACTIONS OF NICKEL CARBONYL WITH OLEFINIC COMPOUNDS YIELDING ISOLABLE COMPLEXES

A. Reaction with Cyclopentadiene and Other Olefins

Chelating olefins such as cycloocta-1,5-diene, cyclooctatetraene, or dicyclopentadiene have not yielded isolable complexes by direct reaction with nickel carbonyl, probably for reasons outlined in Section III, B. From this it should not be concluded that such complexes are incapable of existence. Using reactions in which nickel carbonyl is not the reactant it has been possible to prepare not only complexes of cyclooctadiene and cyclooctatetraene, but also of simple monoolefins (Section IX).

Norbornadiene when heated with nickel carbonyl also does not afford a complex, but is dimerized and carbonylated (Section VIII, C). Cyclopentadiene when refluxed with nickel carbonyl yields red, crystalline (m.p. 41–42°C), volatile, and air-sensitive, π -cyclopentenylcyclopentadienyl-nickel (XIII) (39, 40, 41). This complex may also be obtained from nickelocene by reducing it with sodium amalgam in absolute ethanol (40). The mechanism of its formation from nickel carbonyl is unknown. One might speculate that it is formed via the intermediate (XII)

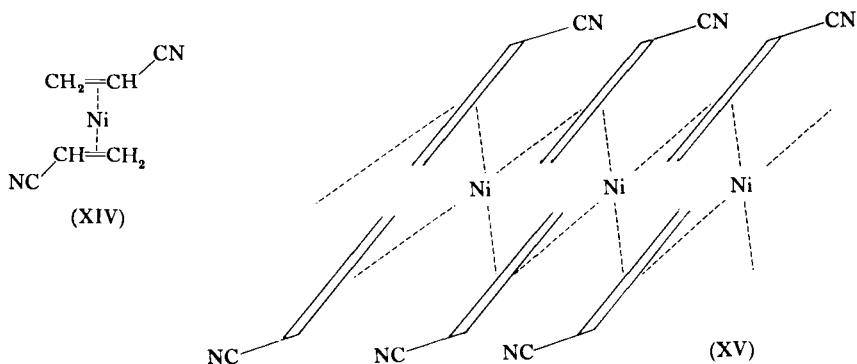


A methyl-substituted compound (XIII) is obtained similarly from nickel carbonyl and methylcyclopentadiene (41a). Analogous to (XIII) is π -allyl-cyclopentadienylnickel, which was prepared from π -allylnickel (II) bromide and sodium cyclopentadienide (41b).

B. Reactions with Vinyl Compounds [Bis(acrylonitrile)-nickel and Derivatives]

1. Bis(acrylonitrile)-nickel

It was observed by the author in 1958 that if nickel carbonyl is refluxed with acrylonitrile in an inert atmosphere all four molecules of carbon monoxide are replaced by two molecules of acrylonitrile and red, crystalline bis(acrylonitrile)-nickel is formed (42). The compound is insoluble in all noncoordinating solvents, as well as being nonvolatile and pyrophoric. It decomposes irreversibly at about 105° into nickel and monomeric acrylonitrile. Spectral evidence unambiguously shows that the nickel atom must be coordinated to the olefinic double bond, and the nitrile groups interact with the metal atom little if at all. For the molecular unit a structure (XIV) was proposed which is also in accord with a more detailed infrared analysis (43). The complex is undoubtedly associated in the solid state, as follows from its physical properties. It is relatively inert to molecular hydrogen. Rhodium-supported hydrogenation catalysts are required to hydrogenate the coordinated acrylonitrile at normal pressure (44). It is possible that the complex has a chain structure with multicenter or metal-metal bonds (or both) between the individual molecules (XV), but it is difficult to assess the detailed nature of such intermolecular interactions without an accurate structural determination. Unfortunately, it is very difficult to grow single



crystals, so that a very interesting structural problem still awaits final solution.

Well-defined 1:1 and 1:2 adducts with triphenylphosphine are formed with ease (42, 45, 46). The yellow 1:1 adduct is more stable than bis(acrylonitrile)-nickel itself (dec. p. 185° C) and represents one of the first examples of a nickel complex with the coordination number three. The 2:1 adduct is monomeric in benzene and has a dipole moment of 6 Debye units (46). Unstable bis(pyridine) adducts were also isolated, but were found to decompose at room temperature, depositing metallic nickel (46).

Owing to the presence of the strongly electronegative CN group, acrylonitrile possesses a low-lying unoccupied molecular orbital which may effectively overlap with a 3*d* orbital of the nickel atom. The question of why acrylonitrile coordinates through the double bond rather than through the

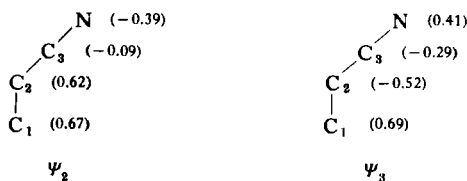


FIG. 1. MO coefficients of the highest bonding (Ψ_2) and the lowest antibonding (Ψ_3) MO's in acrylonitrile. For the parameters used, see ref. (47).

nitrile group may be answered by employing MO theory (47). The MO coefficients of the two most strongly interacting acrylonitrile orbitals (which are the highest occupied and the lowest unoccupied MO's) are particularly large at the olefinic carbon atoms. Consequently, the positions of highest σ -donating and π -accepting strength are localized at the olefinic carbon atoms, which therefore will be the favored coordination sites for the nickel atom (Fig. 1).

Calculations for a monomeric structural unit show that dative π bonding is greatest if the nickel atom interacts symmetrically with the double bond (47). The reason why all four CO molecules are lost by simply refluxing nickel carbonyl with acrylonitrile is a consequence of the significant π bonding ability of this ligand. The replacement of two CO groups by two acrylonitrile molecules would lead to a $\text{Ni}(\text{CO})_2(\text{CH}_2=\text{CHCN})_2$, in which the π bonds would be mainly localized between the nickel atom and the $\text{CH}_2=\text{CHCN}$ molecules, and this would provide insufficient stabilization for the CO groups. For precisely the same reason a complex of composition

$\text{Ni}(\text{H}_2\text{C}=\text{CHCN})_4$ is incapable of existence. The formation of stable mono and bis adducts with phosphines, on the other hand, is to be expected as the latter are mainly σ bonding (37). It was recently found that bis(acrylonitrile)-nickel is not formed if the reaction is performed under moderate carbon monoxide pressure. Evidently carbon monoxide may effectively compete with the acrylonitrile during the substitution process.

The complex (XIV) is diamagnetic. Previously reported small paramagnetic moments have now been recognized as being due to impurities (traces of finely divided metallic nickel) (47).

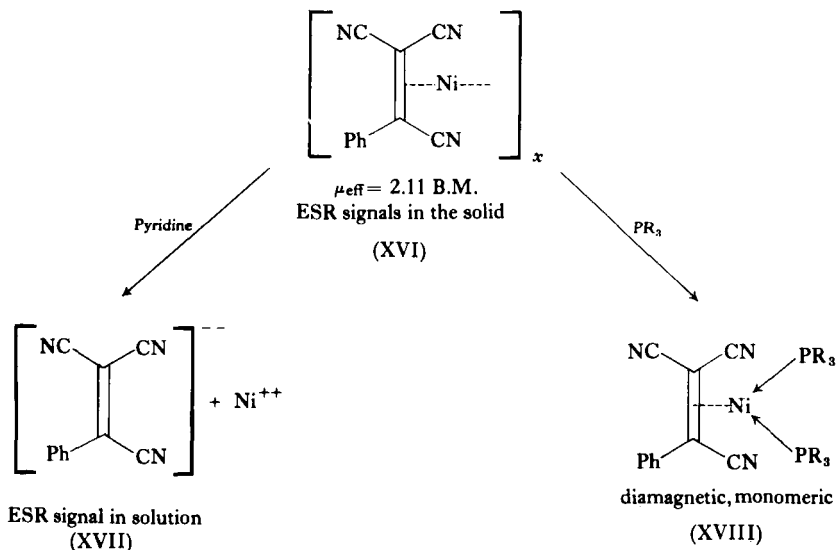
2. Structural Analogs

Complexes analogous to bis(acrylonitrile)-nickel were obtained with cinnamonitrile, fumaronitrile, acrolein, and maleic anhydride. Bis(cinnamonitrile)-nickel is dark violet in color and is somewhat less stable than the acrylonitrile complex (42, 46), whereas bis(fumaronitrile)-nickel appears to be more stable. Both complexes dissolve in bases such as pyridine, forming nonconducting, air-sensitive solutions (46). Bis(acrolein)-nickel is obtained in a manner similar to the acrylonitrile compound and forms deeply violet crystals which decompose at about 90–95°C into nickel and monomeric acrolein (42, 46). In the infrared spectrum (43) the $\text{C}=\text{C}$ stretch is shifted only slightly as compared with liquid acrolein (1616 cm^{-1} in liquid acrolein, 1605 cm^{-1} in the complex), and there is only a small change in the $\text{C}-\text{H}$ out-of-plane vibration. The carbonyl frequency decreases from 1675 to 1518 cm^{-1} upon complex formation. This indicates that the carbonyl group must be very strongly polarized, suggesting strong electron back-donation. It is, however, not known whether the oxygen atoms participate directly in the bonding or not. Bis(acrolein)-nickel also forms adducts with triphenyl phosphine. Its relationship to bis(acrylonitrile)-nickel may be elegantly demonstrated by treating it with acrylonitrile. Even at room temperature acrolein molecules are replaced, and bis(acrylonitrile)-nickel is formed (46). Maleic anhydride forms a complex which resembles bis(fumaronitrile)-nickel in its reactivity, but the compound has not yet been extensively studied (49, 50).

3. Complexes Formed from 1,1-Dicyano- and 1,1,2-Tricyanoethylenes

The unsubstituted 1,1-dicyano- and 1,1,2-tricyanoethylenes are extremely reactive and polymerize when heated with nickel carbonyl. Phenyl-

substituted derivatives of these nitriles, however, react with nickel carbonyl to form complexes. In contrast with acrylonitrile and fumaronitrile, only 1:1 species are formed. This has been attributed to the high electron affinity of these ligands. From spectral data and because of the chemical properties polymeric structures (XVI) were proposed (51). Tetracyanoethylene also reacts with nickel carbonyl but only saltlike ill-defined products were isolated, in which nickel is present in the +2 oxidation state (51, 52).



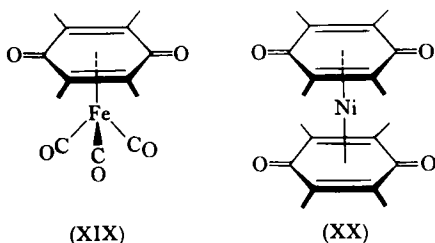
The compounds derived from 1,1-dicyanoethylene, and especially phenyltricyanoethylene, must still be regarded as covalent π complexes although they represent rare examples of compounds practically at the verge of oxidation. Thus in the solid state nickel-phenyltricyanoethylene exhibits ESR signals, indicating that a fraction of the valence electrons of nickel already occupy a low-lying ligand orbital. The complex also is paramagnetic with $\mu = 2.11$ B.M. (51). Both complexes dissolve in various bases, e.g., pyridine or piperidine, forming Ni(II) ions and ligand dianions (XVII); strong ESR signals appear close to the g factor of 2 in such solutions. With tri-*n*-butylphosphine 2:1 adducts (XVIII) are formed. These are diamagnetic and monomeric in benzene. Their infrared spectra establish that they are π complexes in which the nickel atom interacts with the olefinic double bond (51).

V

REACTIONS OF NICKEL CARBONYL WITH QUINONES
AND OLEFINS

A. General Remarks

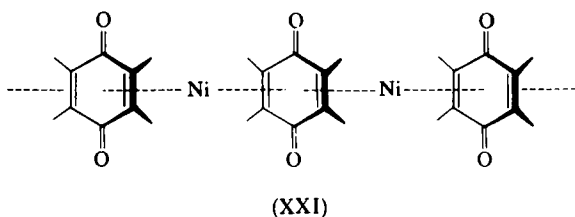
The fact that quinones may form π complexes with transition metals was first recognized by Sternberg *et al.* (53), who found that butyne reacts with iron pentacarbonyl in sunlight to afford duroquinone-iron tricarbonyl (XIX). These authors also reported that manganese pentacarbonyl hydride yields durohydroquinone under similar conditions whereas nickel carbonyl did not react (53a). However, more recent work has established that duroquinone and some other substituted quinones are capable of forming Ni(O) complexes, most of which are surprisingly stable.



B. Bis(duroquinone)-nickel

Most quinones, instead of forming π complexes, react with nickel carbonyl yielding salt like materials. With *p*-benzoquinone, for instance, a nearly black, insoluble, hygroscopic and paramagnetic ($\mu_{\text{eff}} = 3.3$ B.M.) material of composition $\text{Ni}(\text{quinone})_2$ was obtained which is best formulated as $\text{Ni}^{2+}(\text{quinone})_2^{2-}$ and considered as a metallic quinhydrone type of compound (54). However, duroquinone behaves exceptionally. In a smooth reaction all four molecules of carbon monoxide are evolved and red, crystalline, diamagnetic bis(duroquinone)-nickel (XX) (54) is obtained. This complex is stable in air and begins to decompose without melting at 205°C . It is nearly insoluble in all solvents except dichloromethane, in which it is monomeric. In the infrared spectrum, the quinone $\text{C}=\text{O}$ stretching frequency appears at 1577 cm^{-1} (in free duroquinone it is 1629

cm^{-1}), which again suggests extensive electron back-donation to the ligand from nickel. When heated *in vacuo*, it releases one molecule of duroquinone at about 160°C and yields a violet, pyrophoric residue of approximate composition $\text{Ni}(\text{duroquinone})$ (55). This material is insoluble in all common solvents, and is rapidly decomposed by dilute acids to Ni(II) ion and durohydroquinone. Extraction with warm dichloromethane yields bis(duroquinone)-nickel and a nickel-containing residue. From the similarity of its infrared spectrum with that of bis(duroquinone)-nickel, an associated structure (XXI) appears most probable



Since the donor strength of duroquinone is rather small, the capacity of the nickel atom in stabilizing *two* duroquinone molecules by dative π bonding is probably limited. The situation is similar to that in the nickel complexes of the 1,1-dicyano- and 1,1,2-tricyanoethylenes which also form only 1:1 complexes (Section IV, B, 3). During thermal decomposition of (XX) monomeric, coordinately unsaturated “ $\text{Ni}(\text{duroquinone})$ ” is formed. This species is evidently very reactive and rapidly associates to (XXI). It may be trapped in the monomeric state if generated in the presence of electron donors such as cyclic dienes and some phosphines. Under these conditions new complexes of composition olefin- Ni(0) -duroquinone and (phosphine) $_2$ - Ni(0) -duroquinone are formed (55, 56, 57).

C. Complexes of Nickel with Duroquinone and Cyclic Olefins

It was found that if bis(duroquinone)-nickel is thermally decomposed in the presence of cyclooctatetraene, cyclooctatetraene-duroquinone-nickel, (XXII), is obtained (56). A more convenient synthesis was found shortly thereafter in a one-step reaction of duroquinone with nickel carbonyl in the presence of the polyolefin. Using the same procedure, analogous complexes with various other olefins were made, the properties of which are listed in

Table I. Only olefins containing at least two roughly parallel double bonds are suitable as ligands and it follows from the NMR spectra of the complexes that they must have highly symmetrical structures, e.g., (XXIII, XXIV, and XXV) (55, 56). An X-ray structural determination of cycloocta-1,5-diene-duroquinone-nickel has been performed by Glick and Dahl (56a). The space group is $P(2/n)$ with four molecules per unit cell, $a = 14.26$,

TABLE I
PROPERTIES OF DUROQUINONE COMPLEXES OF NICKEL^a

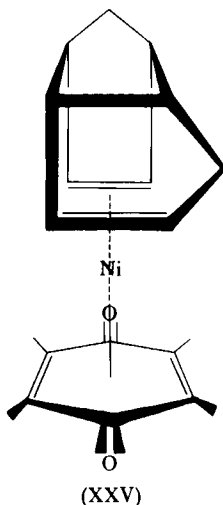
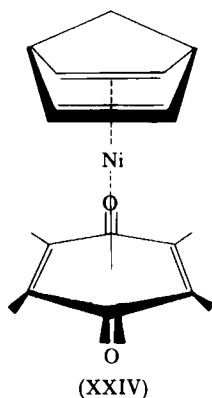
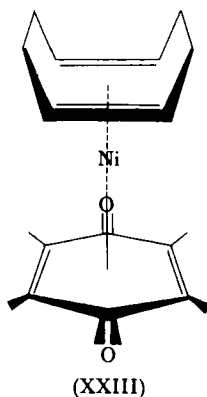
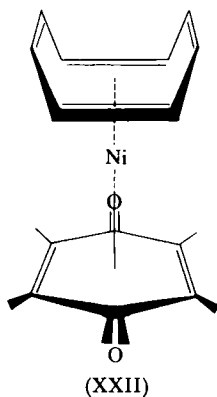
Complex	Dec. p. (°C)	IR C=O (cm ⁻¹)	Dipole moment (Debye)	Color
Bis(duroquinone)-Ni(0)	205	1577	^b	Brick red
Cyclooctatetraene-duroquinone-Ni(0)	165	1553	3.47	Brown-red
Cyclooctatriene-duroquinone-Ni(0)	151-152	1553	3.77	Brown-red
Cycloocta-1,5-diene-duroquinone-Ni(0)	205	1553	4.30	Dark red
Bicyclo(2.2.1)heptadiene-duroquinone-Ni(0)	130	1546	4.07	Brown-red
<i>endo</i> -Dicyclopentadiene-duroquinone-Ni(0)	137	1553	4.23	Brown
Cyclooctatriene-duroquinone-Ni(0)	123-125	1565	^b	Dark red

^a References (55, 56, 58).

^b Dipole moment could not be determined due to insufficient solubility.

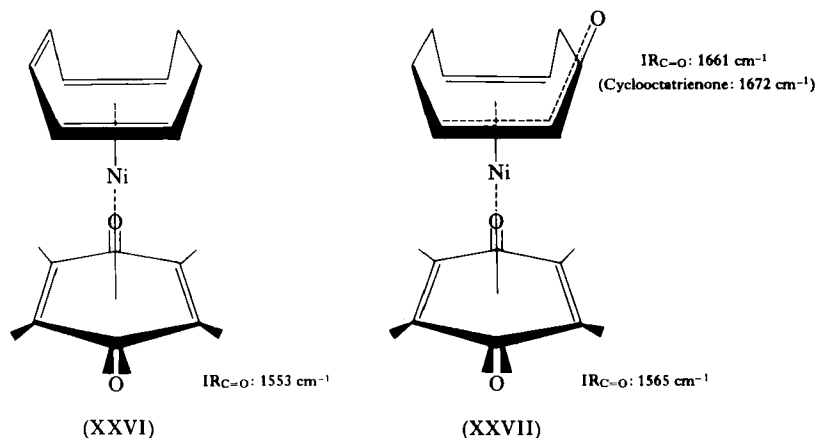
$b = 7.95$, and $c = 14.17$ Å. The nickel is symmetrically bonded to the double bond centers of both the cyclooctadiene and the duroquinone molecules. The arrangement of the four double bonds is such that a tetrahedrally coordinated nickel results. Similar structures may be anticipated for the remaining complexes of the type olefin-duroquinone-nickel.

All complexes of this kind are quite polar and water soluble. The permanent dipole moments are caused by the fact that the olefinic ligands are predominantly donors and only weak acceptors so that the duroquinone molecule interacts with filled $3d$ orbitals of nickel even more strongly than in the case of bis(duroquinone)-nickel. Consequently, the quinone C=O groups are more polarized than in the parent compound bis(duroquinone)-nickel (see Table I). The particularly high stability and polarity of the



cycloocta-1,5-diene complex is undoubtedly due to the favourable steric arrangement of the coordinating double bonds. Cyclooctatetraene, on the other hand, is a weaker donor as the distance between the adjacent double bonds is probably somewhat greater than in cycloocta-1,5-diene. It is instructive to compare the complex of cycloocta-1,3,5-triene with that of cyclooctatrienone. In spite of the nonplanarity of the latter ligand, the presence of the electronegative CO group would be expected to increase slightly the acceptor strength of the olefinic double bonds with respect to cyclooctatriene. This in turn would weaken the dative π bonds from the nickel atom to the duroquinone molecule. The relative positions of the

duroquinone C=O stretching frequencies in both (XXVI) and (XXVII) support this idea.

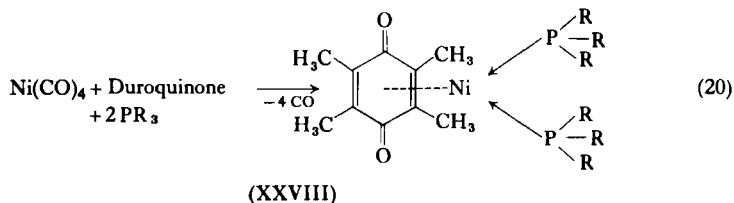


During thermal decomposition of the complexes *in vacuo* the olefinic component is released first and the nickel-quinone (1:1) complex (XXI) is again formed. The olefinic ligands can also be replaced by others, but the exchange reaction will only occur under relatively mild conditions (heating to 80–100° C in the presence of the displacing olefin) if a more stable complex is to be obtained. To convert a stable complex, e.g., cycloocta-1,5-diene-duroquinone-nickel, into a relatively labile one, e.g., bicycloheptadiene-duroquinone-nickel(0), temperatures of more than 120° C are required and yields are poor. From such experiments a stability sequence for the complexes was obtained which parallels the dipole moments (56) (Table I). All complexes are converted into nickel carbonyl at 100 atm of CO and at 60° C, but are recovered unchanged at lower temperatures (59). When an attempt (56) was made to convert bis(duroquinone)-nickel into bis(acrylonitrile)-nickel by treating (XX) with acrylonitrile it was found that this ligand rapidly decomposes the duroquinone complex with simultaneous formation of nickel-containing polyacrylonitrile. It has been suggested that this polymerization is initiated by the monomeric Ni(duroquinone) (56).

All the duroquinone-nickel complexes are diamagnetic. Attempts to prepare similar compounds with *o*-quinones have failed. It is also impossible to prepare bis(trimethylquinone)-nickel. Instead, the Ni(II) salt of trimethylquinone is isolated (58). Evidently a slight increase in the electron affinity of the quinone π system is sufficient to induce oxidation of nickel.

D. Complexes of Nickel with Duroquinone and Phosphines

The reaction of nickel carbonyl with duroquinone in the presence of an excess of triphenylphosphine produces the insoluble Ni(duroquinone). The same reaction in the presence of tri-*n*-butylphosphine, however, yields red, crystalline air-sensitive bis(tributylphosphine)-duroquinone-nickel (XXVIII), Eq. (20), (57).



E. Complexes with Other Quinones

When *p*-benzoquinone or toluquinone are treated with nickel carbonyl in the presence of cycloocta-1,5-diene only Ni(II)-hydroquinone or quinhydrone salts, respectively, are formed. When the somewhat less strongly oxidizing 2,5- or 2,6-dimethyl quinones are treated with nickel carbonyl under the same conditions cycloocta-1,5-diene-dimethylquinone-Ni(0) complexes are obtained. These substances resemble their duroquinone

TABLE II

C=O STRETCHING FREQUENCIES AND DECOMPOSITION POINTS OF CYCLOOCTA-1,5-DIENE-NICKEL COMPLEXES OF SOME QUINONES^a

Quinone	CO stretching frequency (cm ⁻¹)		Dec. p. (°C)
	In the free quinone	In the complex	
Duroquinone	1629	1553	205
Trimethylquinone	1650	1574	118-120
2,5-Dimethylquinone	1664	1580	150
2,6-Dimethylquinone	1654	1570	109-110
<i>d,l</i> - α -Tocopherylquinone	1647	1533	100

^a References (58, 59).

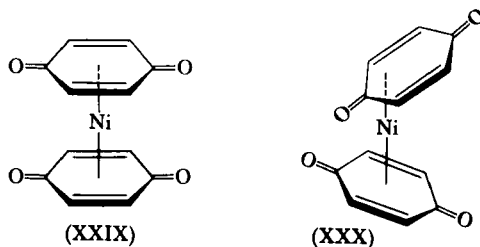
analog. 2,3-Dimethylquinone, however, oxidizes the nickel atom. The analogous trimethylquinone-nickel complex of cycloocta-1,5-diene has been prepared and has a dipole moment of $4.78D$ in benzene solution (58). All these complexes are readily soluble in water, but are somewhat less stable than the corresponding duroquinone complexes. Aqueous solutions are yellow-red and nonconducting. The $C=O$ infrared stretching frequencies and decomposition points are listed in Table II.

It is worth mentioning that the first transition metal complex of a natural product was obtained by treating tocopherylquinone (vitamin-E-quinone) with nickel carbonyl in the presence of cycloocta-1,5-diene. A study of its physiological properties promises to be interesting (59).

F. Electronic Structure, Spectra, and Magnetism of Quinone Complexes of Nickel

1. Bis(duroquinone)-nickel

Molecular Orbital Theory has been applied (60) to complexes of the type duroquinone- $Fe(CO)_3$ and has also been used for bis(duroquinone)-nickel (61). The calculation was performed for the two possible symmetries, D_{2h}



(XXIX) and D_{2d} (XXX), respectively. From the magnitude of the calculated overlap integrals it follows that dative π bonding must be quite strong. Adopting the energetical sequence of the quinone MO's

$$1b_{1u} < 1b_{2g} < 2b_{1u} < b_{3g} < 2b_{2g} < 1a_u < 3b_{1u} < 3b_{2g} \quad (62)$$

it is concluded that for energetical reasons the interactions $2b_{1u}-4s/4p_z$, $b_{3g}-3d_{yz}/4p_y$, and $2b_{2g}-3d_{xz}/4p_x$ will be the most important. The first two correspond to the coordinative σ and π bonds and the last to the dative π bond. As the $2b_{2g}$ orbital is at low energy significant charge transfer from the nickel atom to the quinone molecule is to be expected. Depending on

the electron affinity of the quinone, this may become so strong that the nickel atom is oxidized and only saltlike products are formed. The presence of the four CH_3 groups in duroquinone, however, lowers the electron affinity of the quinone π system to such an extent that a π complex may exist. For the twenty-six available electrons twelve bonding or relatively low energy nonbonding MO's may be used. Two electrons must be placed in an antibonding orbital, localized mainly on the nickel atom. This is expected to lower the stability of the complex and lead to a longer metal-, ring distance. Similar results are obtained for D_{2d} symmetry of the complex, in which four electrons would have to occupy an antibonding doubly degenerate metal orbital. For both (XXIX) and (XXX), however, the same total orbital stabilization results. Simple MO theory thus does not allow any predictions as to which of the two structures will be assumed.

2. Olefin-Quinone-Nickel Complexes

Complexes of this type have been treated assuming C_{2v} symmetry for the molecule, e.g., cycloocta-1,5-diene-duroquinone-nickel (61). It is possible to place twenty of the twenty-two electrons into ten bonding or virtually nonbonding orbitals. However, again two electrons must occupy an antibonding level. Owing to the absence of similar low-lying orbitals in the olefinic ligands, dative π bonding will be largely restricted between the metal and the quinone, causing an unsymmetrical charge distribution in these complexes.

3. Electronic Spectra

Spectra of some of the complexes are given in Fig. 2. The three characteristic absorptions in the spectra of quinones have been assigned to $n \rightarrow 2b_{2g}$, $b_{3g} \rightarrow 2b_{2g}$, and $2b_{1u} \rightarrow 2b_{2g}$ -transitions, respectively (62). It follows from the calculated orbital energies in the complexes (61) that the $b_{3g} \rightarrow 2b_{2g}$ -transition should be shifted to higher energies upon complex formation, whereas the remaining quinone transitions would remain almost unaffected. This indeed has been found to be the case. Experimental term-level schemes are given in Fig. 3. In addition to the quinone transitions, a new band is observed which was assigned to a charge transfer transition from the highest filled nickel orbital to the lowest unoccupied MO in the complexes. A duroquinone complex of cobalt, duroquinone-cyclopentadienylcobalt was recently prepared and found to have a very similar term-level scheme (64). Transitions

involving the olefinic components in complexes of the type olefin-duroquinone-nickel have not been observed. They are expected to occur at shorter wavelengths and may be partly covered by the intense quinone

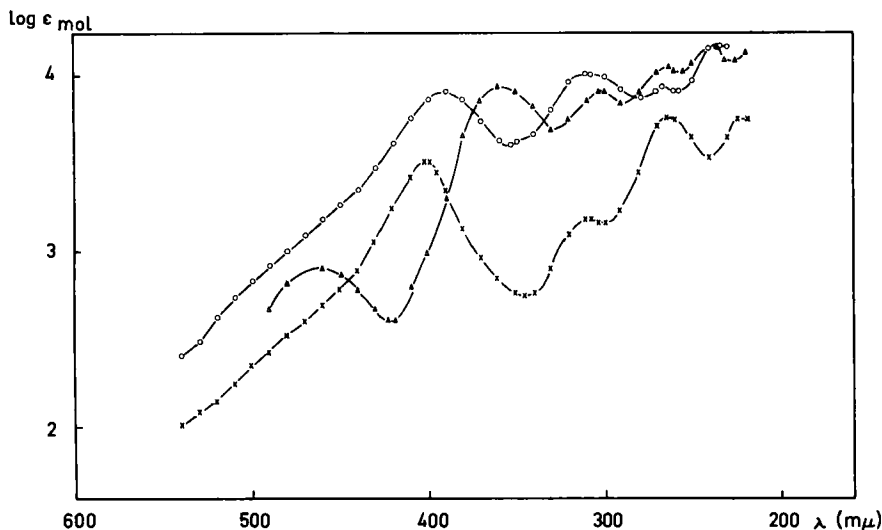


FIG. 2. Electronic spectra of some duroquinone-Ni(0) complexes, recorded in methanol solution (63). $\times-\times-\times$ Bis(duroquinone)-nickel; $\Delta-\Delta-\Delta$ cyclooctadiene-duroquinone-nickel; $\circ-\circ-\circ$ norbornadiene-duroquinone-nickel.

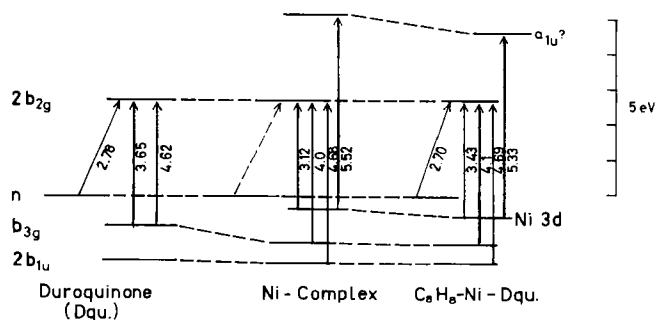


FIG. 3. Experimental term-level schemes for duroquinone, bis(duroquinone)-nickel, and cyclooctatetraene-duroquinone-nickel (61).

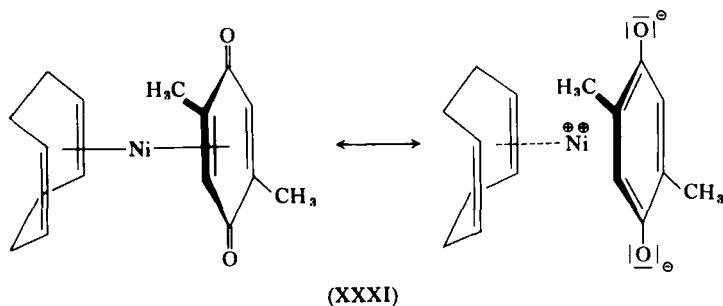
transitions. In cyclooctatrienone-duroquinone-nickel, however, such transitions have been observed, as this cyclic ligand absorbs at longer wavelengths than unsubstituted cycloolefins.

Application of the quantum mechanical selection rules to the transitions

in bis(duroquinone)-nickel revealed that for D_{2d} symmetry of the complex all transitions are allowed, whereas for D_{2h} the transition corresponding to $b_{3g} \rightarrow 2b_{2g}$ in the isolated quinone molecule should remain symmetry forbidden. As the intensity of this transition is found to be comparatively low, it has been concluded that bis(duroquinone)-nickel has D_{2h} symmetry. In the olefin-duroquinone-nickel complexes all quinone transitions are allowed and appear with high intensity. This symmetry assignment may be incorrect in view of the observed structure of cycloocta-1,5-diene, duroquinone-nickel (see Section V, C), and symmetry D_{2d} , with a tetrahedral nickel atom, now appears more probable.

4. Magnetic Properties

According to the MO treatment, all duroquinone complexes should have a singlet ground state and should be diamagnetic. This has been confirmed by experiment. However, the cycloocta-1,5-diene complexes of Ni with 2,5- or 2,6-dimethylquinone are paramagnetic in the solid state with moments of 1.5 and 2.75 B.M., respectively (64). If it is assumed that the total wave function for these complexes already contains ionic contributions, as indicated by (XXXI), it is probable that intramolecular oxidation takes place, causing the observed magnetic moments.

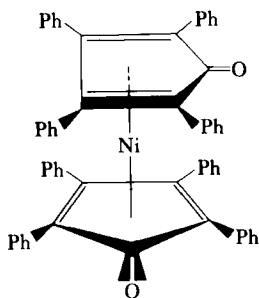


VI

REACTION BETWEEN NICKEL CARBONYL AND ACETYLENES WHICH YIELD COMPLEXES

Reactions between nickel carbonyl and acetylenes which afford isolable complexes are rare. Diphenylacetylene is exceptional in that it yields nearly

black, diamagnetic, unreactive bis(tetracyclone)-nickel (11). This complex may also be prepared directly from tetracyclone and nickel carbonyl. In its infrared spectrum the C=O stretch appears at 1597 cm^{-1} (in free tetracyclone it is 1715 cm^{-1}). This significant decrease in frequency shows that electron back-donation must be stronger than in the tricarbonyliron complexes of tetracyclone, in which the same band appears at 1642 cm^{-1} .



(XXXII)

VII

POLYMERIZATION OF ALKYNES BY PHOSPHINE-NICKEL CARBONYLS

In 1940 Reppe and Schweckendieck discovered that phosphine-substituted nickel carbonyl complexes could catalyze the cyclization of acetylenes (2, 65). This work has recently been extended by several groups of workers. An excellent review summarizing this topic has been written by Hübel and Hoogzand (66), and this article is warmly recommended to the reader. To avoid duplication we will only summarize briefly the present state of this field.

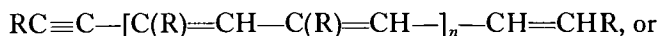
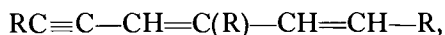
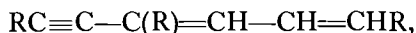
A. Reaction Conditions and Scope

In order to initiate the polymerization reaction, catalyst pretreatment is necessary. Various methods have been suggested, e.g. warming the solution to $100\text{--}110^\circ\text{C}$ in the presence of acetylenes, or agitating the reaction mixture by stirring (2, 67). The main reaction during the catalyst development is the evolution of carbon monoxide. Evidently a labile nickel-phosphine-acetylene complex is formed. With this pretreated catalyst the trimerization

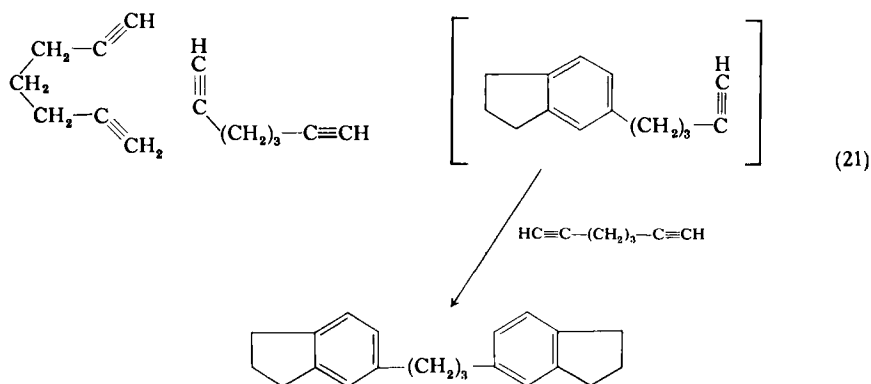
of acetylene proceeds readily at temperatures of 60–70°C and 15 atm of acetylene, yielding benzene and styrene in about 88% and 12% yield respectively (2, 65). A large number of monosubstituted but only a few disubstituted acetylenes may be cyclized similarly.

A detailed study of such reactions has been made by Meriwether *et al.* (67–70). The ability of monosubstituted acetylenes to form benzene derivatives depends on the substituent, and decreases from methyl to *n*-pentyl, indicating a steric effect. Linear oligomers are often formed as by-products. Monosubstituted alkynes carrying bulky groups, e.g. cyclohexylacetylene, yield only a linear dimer, whereas *t*-butylacetylene fails to react at all. The influence of the substituents is of course not only a steric one. Thus the yields of desired aromatic decrease in the sequence $R = -COOR, -OR, COR, -CH_2OH, -CH=CH_2, -Ph, -Me$, and *n*-pentyl. This sequence is difficult to interpret, although it would appear that the presence of polar groups generally facilitates trimerization. However, cyanoacetylene reportedly does not trimerize (67).

Less reactive 1-alkynes yield linear oligomers more readily than benzene derivatives. The chain lengths of the products varied from two to seven. Usually mixtures of several isomers are obtained, e.g.,



Insertion of the alkyne molecules appears to be exclusively *cis*. Most disubstituted acetylenes were found to be unreactive (e.g. 2-butyne, 3-hexyne, tolane, 2,5-dimethyl-3-hexyne-2,5-diol, 3,6-dimethyl-4-octyne-3,6-diol, 1,4-dichloro-2-butyne, 2-butyne-1,4-dioldiacetate, diethylacetylene dicarboxylate, and phenylpropionic acid). Butyne-1,4-diol is exceptional in forming high yields of hexamethylolbenzene (67, 71). Disubstituted conjugated diacetylenes also failed to react, but terminal unconjugated diacetylenes with the complex $Ni(CO)_2 \cdot 2P(C_6H_5)_3$ yielded both high and low molecular weight polymers and aromatic ring structures (69)



Co-trimerization of the unreactive disubstituted acetylenes with acetylene proved possible in some cases. For instance, acetylene with 2-butyne produced benzene, *o*-xylene (72), tetramethylbenzene (67), and styrene (72, 67). Acetylene and divinylacetylene yielded mainly *o*-divinylbenzene (73, 74). The co-trimerization of acetylene with vinylacetylene yielded styrene (75). This reaction probably also accounts for formation of styrene during cyclotrimerization of acetylene, because small amounts of vinylacetylene are usually present or are formed from acetylene under the reaction conditions.

B. Mechanism of Formation of Linear Polymers

When deuterated 1-heptyne was polymerized it reacted at a considerably slower rate than the undeuterated species (70). Meriwether *et al.* conclude from this important effect that cleavage of a carbon-hydrogen bond determines the rate and that only one hydrogen transfer is involved in the formation of product. They assume intermediate σ -bonded species containing Ni—H and Ni—C bonds (XXXIII), (XXXIV), and (XXXV), (Fig. 4).

There is evidence for the intermediate formation of nickel hydride-acetylides in the polymerizations. Addition of $\text{Ni}(\text{CO})_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$ to a mixture of 1-heptyne-1-*d* and 1-pentyne leads to a rapid deuterium exchange after an induction period (70). Rate-determining steps for this transition metal-assisted deuterium-hydrogen exchange are considered to be the termination and the catalyst recovery processes which involve the transfer of a hydrogen atom and the cleavage and formation of a new Ni—C

bond. The suggested mechanism for linear oligomerization of alkynes thus reflects current mechanistic ideas on Ziegler-Natta polymerization reactions (70). However, some doubt must be cast on the assumed structure of some of the intermediate complexes.

Reactions between alkynes and phosphine-nickel carbonyl complexes show a remarkable insensitivity toward the solvent and may be performed

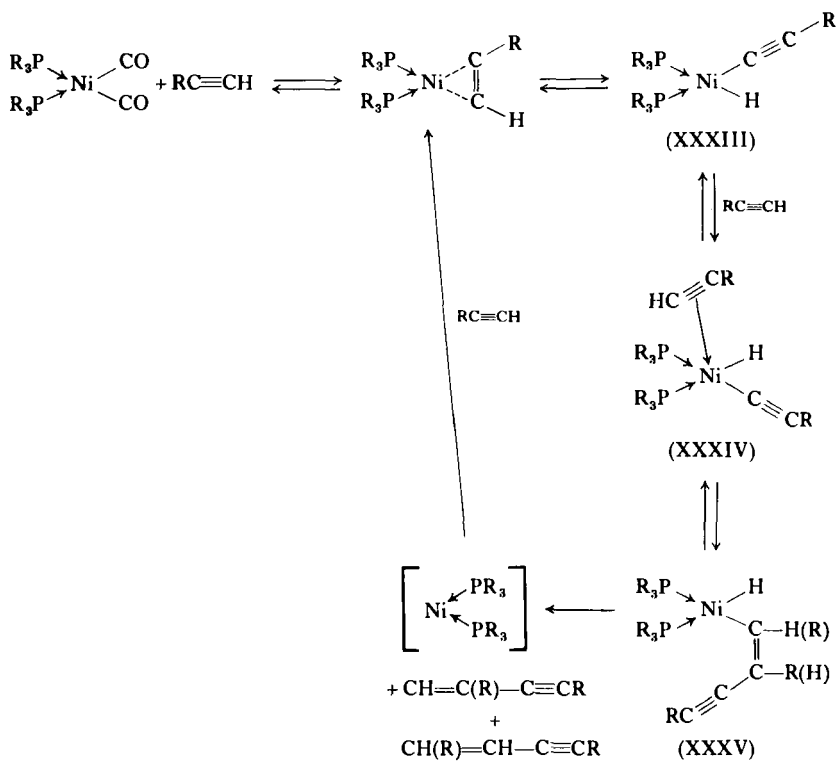


FIG. 4. Assumed mechanism of formation of linear oligomers by treating mono-substituted alkynes with Reppe catalysts (70).

in methanol, ethanol, cyclohexane, benzene, dimethylformamide, or acetonitrile without any essential difference in rate. It is difficult to see why this should be so, if the intermediate complexes are indeed square planar complexes of Ni(II) as has been suggested (70). It is interesting to note that the complexes $\text{Ni(CO)}_3\text{PR}_3$ and $\text{Ni(CO)}_2 \cdot 2\text{PR}_3$ hardly differ from each other in their catalytic efficiency and that chelating phosphines as substituents in the nickel carbonyl complexes have no inhibiting effects (70).

C. Mechanism of the Aromatization Reaction

Meriwether *et al.* (70) also proposed a mechanism for the aromatization reaction, shown in Fig. 5. According to these workers formation of benzene derivatives would necessitate migration of hydrogen atoms. Since some disubstituted alkynes may also be cyclotrimerized with phosphine-nickel carbonyl catalysts, this mechanism is less probable.

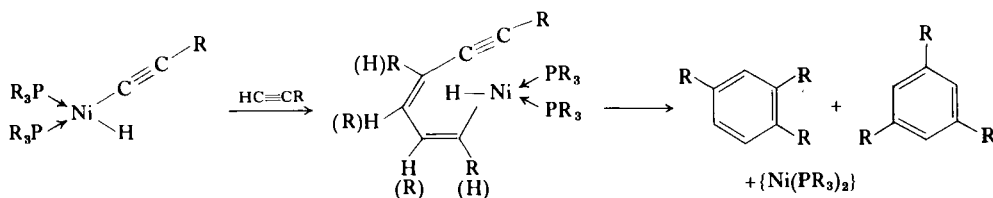


FIG. 5. Proposed mechanism of formation of benzene derivatives (70).

VIII

CATALYTIC REACTIONS OF BIS(ACRYLONITRILE)-NICKEL AND DERIVATIVES

A. General Remarks on Transition Metal-Catalyzed Reactions of Alkynes

Reactions between alkynes and transition metal compounds yield a surprising variety of products (76, 77), indicating nonspecific mechanisms of formation. At least for the reaction of alkynes with metal carbonyls any simple polar mechanism must be excluded, in view of the insensitivity of the reactions to the degree of polarity of the solvents. A radical mechanism would perhaps be better suited for a general description but this has so far been rejected, since inhibition of the reactions with *t*-butylphenol or hydroquinone proved unsuccessful (78). Likewise, iron carbonyls react with diphenylacetylene, using ethyl acrylate, vinyl methyl ketone or vinyl acetate as the solvent, without polymerization of the vinyl compounds (79). These experiments, however, do not fully eliminate the possibility of a radical mechanism.

We have recently found (79a) that during polymerization of both mono- and disubstituted acetylenes with a large variety of catalysts [e.g., phosphine substituted nickel carbonyls, nickelous cyanide, bis(acrylonitrile)-nickel,

nickel acetylacetonate, bis(salicylaldehyde)-nickel, $\text{Fe}_3(\text{CO})_{12}$, $\text{Co}_2(\text{CO})_8$, $\text{Mn}_2(\text{CO})_{10}$ or $\text{PdCl}_2 \cdot 2\text{C}_6\text{H}_5\text{CN}$] *electron resonance signals* with *g* factors of about 2.0028 are detected if the viscosity of the reaction medium is kept high. Nevertheless, it is difficult to assess the mechanistic significance of the observation and a more detailed study of this effect is necessary. At any rate the fact that radicals are produced in transition metal-catalyzed alkyne polymerizations indicates the dramatic activation of the acetylenic carbon atoms in such reactions.

Acetylenes are *a priori* electron-donating ligands with only weak acceptor properties and their π complexes should be relatively labile. The initial step of at least some of the reactions could be a conversion of the complexed acetylene in its ground state to a biradical with sp^2 hybridized carbon atoms. This "activated" acetylene complex may then stabilize itself in many ways, depending largely on the type of the additional coordinated ligands in the transition state.

Longuet-Higgins and Orgel (80) predicted that two π -bonded acetylene molecules should combine to form a cyclobutadiene complex, a proposal which was brilliantly confirmed (81). The formation of four-membered rings, however, occurs only relatively rarely, and many different ways in which π -complexed acetylenes react have become known.

Two limiting cases may be distinguished: In certain simple cases, particularly if cyclic reaction products are formed it is possible to assume that the new C—C bonds are closed simultaneously. Such reactions could be properly described as " π -complex multicenter processes" (79). The linear polymerization of alkynes in which the new C—C bonds cannot be formed simultaneously may be considered the other extreme possibility, but it must also be expected that there are intermediate cases between these two types of reaction. In view of the generally nonspecific action of the catalysts any generalizations must be treated with caution. The reactions of alkynes and of norbornadiene with bis(acrylonitrile)-nickel and related complexes, however, appear to be simple enough to allow some mechanistic conclusions.

B. Reactions with Alkynes

Bis(acrylonitrile)-nickel is coordinately unsaturated and may be expected to add two acetylene molecules, forming intermediate 2:1 adducts of composition $\text{Ni}(\text{CH}_2=\text{CHCN})_2 \cdot (\text{alkyne})_2$. The coordinated ligands (Fig. 6)

could condense, in a fashion which will not be further specified, to form a benzonitrile derivative and a "fragment," $\text{Ni}(\text{CH}_2=\text{CHCN})$. The latter might add three more alkyne molecules to form a complex $\text{Ni}(\text{CH}_2=\text{CHCN})(\text{alkyne})_3$, which could produce a benzene derivative. These possibilities have been verified by treating bis(acrylonitrile)-nickel with diphenylacetylene, thereby affording 1,2,3,4-tetraphenylbenzonitrile and hexaphenylbenzene (79). Bis(acrolein)-nickel behaves similarly, producing tetraphenylbenzaldehyde. With acetylene, heptatrienenitrile (XXXVIII), benzene, and cyclooctatetraene are obtained in approximately

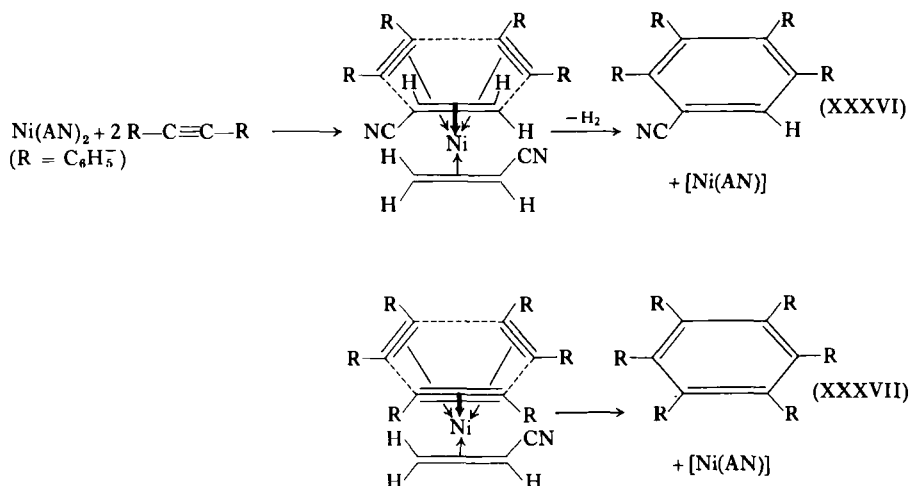


FIG. 6. Schematic representation of the reaction between bis(acrylonitrile)-nickel and diphenylacetylene (79).

stoichiometric yields (Fig. 7). The reaction of acetylene with bis(acrylonitrile)-nickel is not catalytic. During reaction, the π -bonded acrylonitrile molecules are displaced by acetylene molecules. The final intermediate complex would have the composition $\text{Ni}(\text{C}_2\text{H}_2)_4$ and could decompose into nickel and cyclooctatetraene. The nickel atom evidently cannot be resoluted by acetylene and the reaction comes to an end.

The reactions of bis(acrylonitrile)-nickel with acetylene do become catalytic if performed in the presence of triphenylphosphine (79). Under these conditions benzene is formed in excellent yields, using only small amounts of catalyst. Benzene formation has been accounted for by the scheme shown in Fig. 8 (79). Similar schemes to explain the formation of benzene derivatives have been used by other authors, especially Zeiss (77).

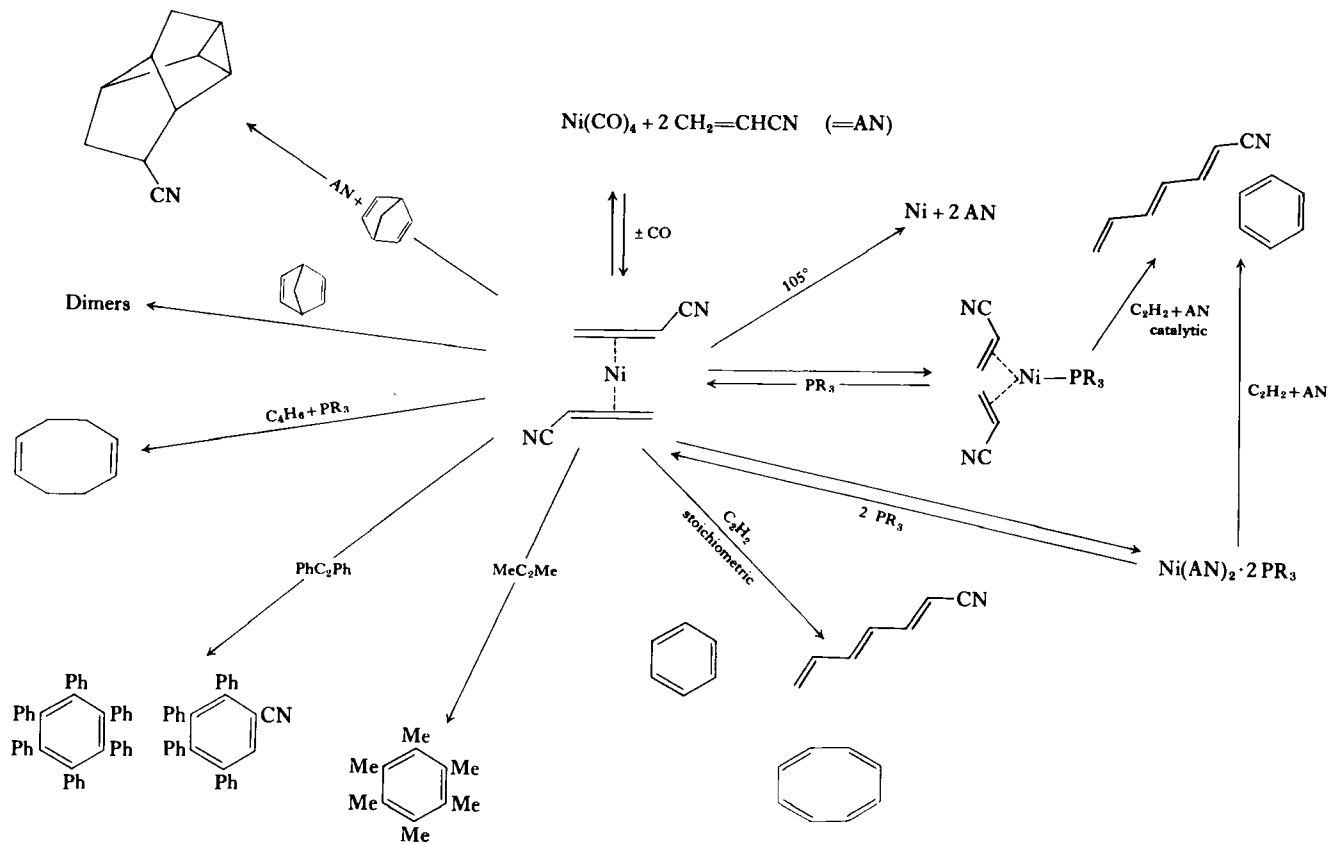


FIG. 7. Some reactions of bis(acrylonitrile)-nickel.

Triphenylphosphine stabilizes the nickel atom by forming a complex. As it blocks at least one of the coordination positions on the nickel atom, only three acetylene molecules may add to it, thus making the formation of cyclooctatetraene impossible (79). Complexes of nickel with 1,1-dicyano- and 1,1,2-tricyanoethylene behave similarly, yielding approximately stoichiometric quantities of benzene and cyclooctatetraene C_8H_8 , but affording exclusively benzene in the presence of triphenylphosphine (51, 82). The original catalysts for Reppe's (2, 83) cyclooctatetraene synthesis were all

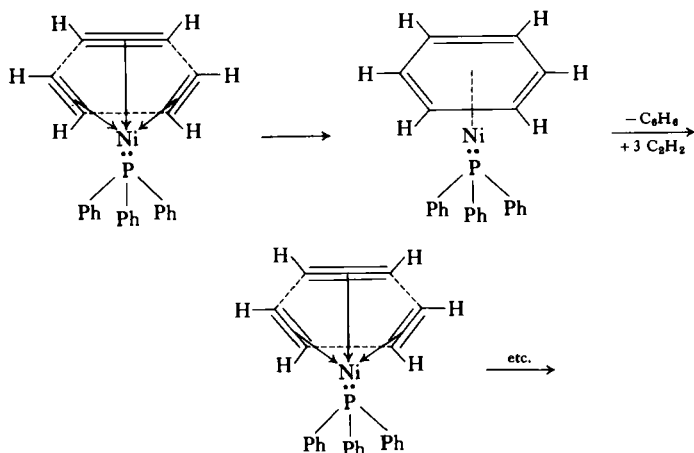
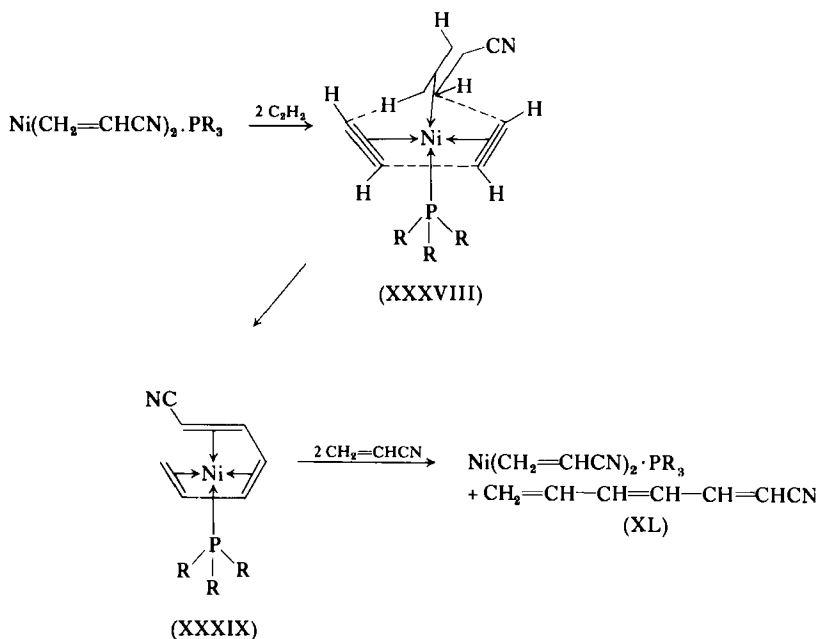


FIG. 8. Suggested mechanism of benzene formation.

Ni(II) complexes. They are indeed much more effective and their function is different (84, 85).

Treatment of propiolic esters with catalysts of the type $Ni(PX_3)_4$ affords small amounts of tetrasubstituted cyclooctatetraenes in addition to benzene derivatives. This is the only other reported instance of cyclotetramerization of an alkyne using a Ni(0) catalyst (86). The synthesis of heptatrienenitrile was discovered in 1952 by Cairns *et al.* (87). These authors treated acetylene with acrylonitrile in the presence of phosphine-substituted nickel carbonyls. Under these conditions the reaction requires an induction period during which bis(acrylonitrile)-nickel and/or its phosphine adducts are formed. Bis(acrylonitrile)-nickel in the presence of triphenylphosphine is now known to be immediately reactive under similar conditions (42). Formation of (XL) must involve a hydrogen shift, and may proceed according to Eq. (22)

Acrylonitrile can be replaced by acrylic esters in these processes (86). It is difficult to explain why these reactions afford only linear condensation products and not aromatic or cycloolefinic compounds. Bis(acrylonitrile)-nickel also reacts with 2-butyne (78) and hexafluorobutyne (88), forming the corresponding benzene derivative and linear oligomers and polymers, respectively. Since phosphine-modified nickel carbonyls usually fail to



(22)

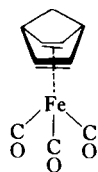
trimerize disubstituted acetylenes (see Section VIII), these results clearly show that the catalytic activity of the nickel atom strongly depends on the nature of the additional ligands attached to it.

C. Reactions with Olefins

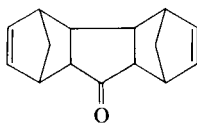
Bis(acrylonitrile)-nickel catalyzes the dimerization of butadiene to cyclo-octa-1,5-diene in the presence of phosphites (89). Catalytic condensations of butadiene, however, will be discussed in Section IX. Of particular interest are reactions of bis(acrylonitrile)-nickel with norbornadiene. This highly

strained diene is known to react with iron carbonyls forming complex (XLI) (90, 91), as well as the cyclic ketones (XLII), (XLIII), and (XLIV) (90). With nickel carbonyl under carbonylation conditions, bicyclo(2.2.1)-heptenecarboxylic ester (XLV) and the ketone (XLVI) are isolated (90). In inert solvents dimerization to the products (XLVII-L) occurs (90, 92, 93).

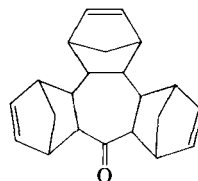
Bis(acrylonitrile)-nickel dimerizes norbornadiene at about 60° to (XLVII) and (XLVIII). In addition small amounts of the nitrile (LI) (see Fig. 9) may also be isolated, suggesting that the coordinated acrylonitrile reacted with the norbornadiene as well. The complexes of 1,1-dicyano- and 1,1,2-



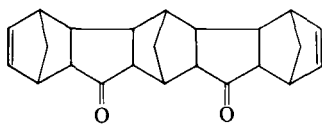
(XLI)



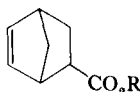
(XLII)



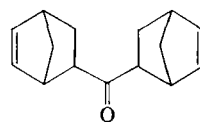
(XLIII)



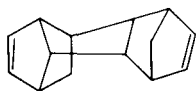
(XLIV)



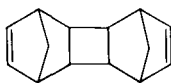
(XLV)



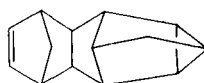
(XLVI)



(XLVII)



(XLVIII)



(XLIX)



(L)

tricyanoethylene are somewhat less active than bis(acrylonitrile)-nickel but afford larger yields of the dimer (XLVIII) and, in addition, the dimer (XLIX) (94). This suggests that the structure of the catalytically active fragments (in this case, the complexes themselves), affects the nature of the

reaction products (94). Bis(fumaronitrile)-nickel is practically incapable of promoting the dimerization of norbornadiene. At 120° C only traces of dimers are obtained (94). This is undoubtedly because of its higher stability. In the presence of acrylonitrile, no dimers are produced and the nitrile

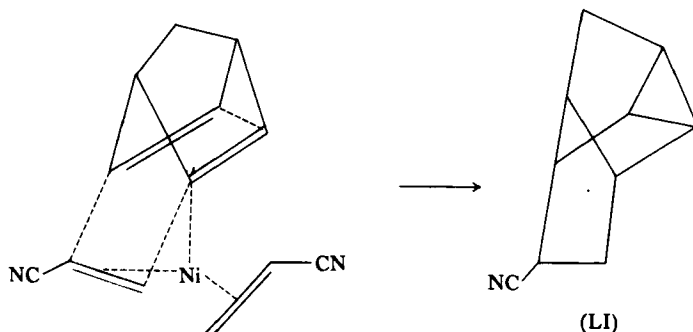


FIG. 9. Reaction of bis(acrylonitrile)-nickel with norbornadiene (94).

(LI), 6-cyanotetracyclo(3.2.1.1.0)nonane, is isolated in 95% yield [with bis(acrylonitrile)-nickel as catalyst]. This is the first case of a transition metal-catalyzed transannular addition. It may be formulated according to Fig. 9 and provides a good example of a π -complex multicenter process.

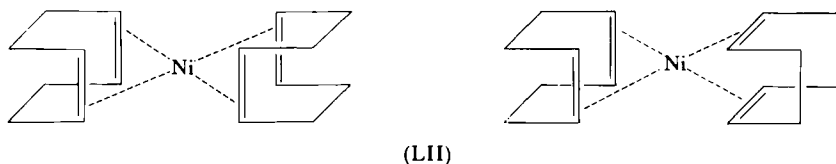
IX

CATALYTIC CYCLIZATION OF DIENES WITH NEW π COMPLEXES OF NICKEL

A. Bis(cycloocta-1,5-diene)-nickel

The thermal polymerization of butadiene yields, according to Ziegler *et al.*, a mixture of vinylcyclohexene with at most 15% of cyclooctadiene (95, 96). In 1954 Reed (97) discovered the catalytic cyclodimerization of butadiene to cycloocta-1,5-diene with Reppe catalysts, with a 30–40% conversion at 120–130° C. Wilke *et al.* recently synthesized a very efficient class of catalyst. If nickel-acetylacetonate is treated with metal alkyls (especially aluminum alkyls) in the presence of electron-donating compounds (mainly cycloolefins), new π complexes of nickel are obtained which catalyze the cyclo-oligomerization of butadiene (98, 99). Using cycloocta-1,5-diene as the olefinic component, the well-crystallized, faintly yellow bis(cycloocta-

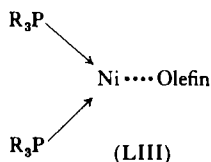
diene)-nickel, (LII), is obtained. This is the first π complex formed by nickel with a simple olefinic ligand. Spectral evidence shows that both cyclooctadiene molecules are symmetrically coordinated to the nickel atom. From a comparison of the infrared with the Raman spectrum it has been concluded that the molecule lacks a center of symmetry, suggesting that the nickel atom is in the sp^3 state of hybridization (100).



Since cyclooctadiene has no suitable low-lying unoccupied orbitals some of the $3d$ electrons of nickel are expected to have a relatively high antibonding character. It is therefore not surprising that the nickel complex is extremely reactive, air-sensitive, and very unstable in solutions even in the absence of oxygen. Carbon monoxide at room temperature completely displaces the cyclooctadiene molecules and yields nickel carbonyl (99). Acrylonitrile reacts with (LII) under similarly mild conditions, forming bis(acrylonitrile)-nickel (101), while duroquinone, well below room temperature, affords cyclooctadiene-duroquinone-nickel (101). These reactions uniquely demonstrate the close interrelationship between all complexes of zero-valent nickel.

B. Complexes of the Type $(\text{Phosphine})_2\text{Ni}(\text{Olefin})$

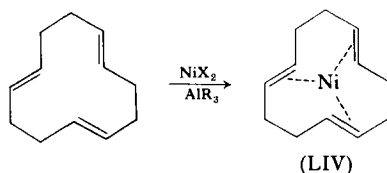
Reduction of nickel acetylacetonate in the presence of phosphines and olefins produces complexes of zero-valent nickel with the coordination number three. The ligands in (LIII) may be replaced by others under mild



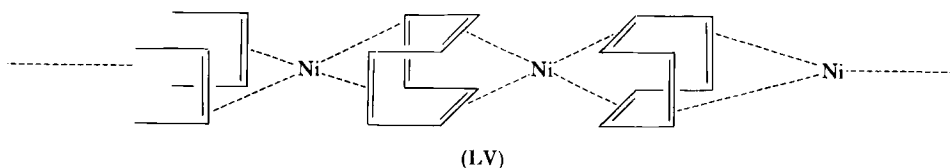
conditions. Complexes of ethylene styrene, methylstyrene, stilbene, tolane, 2-butyne, and triethylphosphine as ligands have reportedly been prepared but have not yet been described in detail (99).

C. Cyclododecatriene-nickel and Complexes of Cyclooctatetraene

Perhaps the most important complex of this series is cyclododecatriene-nickel, readily obtainable by reducing nickel-acetylacetonate with aluminum alkyls in the presence of cyclododecatriene. This complex (LIV) forms blood-red needles, is sublimable *in vacuo*, and is monomeric in the vapor phase (99). It is coordinately unsaturated and, being only a sixteen-electron complex, it not surprisingly reacts with carbon monoxide at -80°C , forming a monocarbonyl which is colorless and decomposes at 20°C into cyclododecatriene, nickel, and nickel carbonyl. More stable adducts are produced with phosphines which, due to their stronger σ -bonding character, will increase the electronic density on the nickel atom and thus favor π bonding to the olefinic ligand. It is still unknown whether the nickel atom is in a triangular environment or not. Although sp^2 -hybridized nickel would be more strongly π bonding it is possible that the available cavity in the cyclododecatriene molecule may be too small to allow a completely planar arrangement. Cyclododecatriene-nickel easily undergoes ligand replacement reactions. With cycloocta-1,5-diene it yields bis(cyclooctadiene)-nickel. With cyclooctatetraene at -40°C a relatively unstable complex considered to be bis(cyclooctatetraene)-nickel is formed. This substance decomposes at 20°C into nearly black, sparingly soluble, and probably polymeric cyclooctatetraene-nickel (LV) (99). Complex (LV) may also be obtained by treating bis(cyclooctadiene)-nickel with cyclooctatetraene. It reacts with hydrogen yielding metallic nickel and cyclooctane, and with carbon monoxide to produce nickel carbonyl and cyclooctatetraene. Cyclododecatriene-nickel reacts instantly with hydrogen due to its coordinative unsaturation, whereas bis(cyclooctadiene)-nickel requires an induction period. Hydrogenation of the latter appears to take place only in the presence of small amounts of free nickel (99).

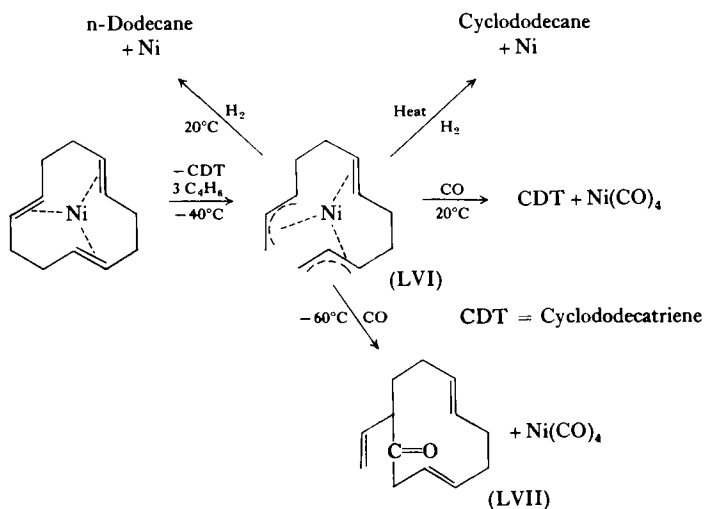


Complex (LIV) is extremely air-sensitive but is unaffected by deoxygenated water. This suggests that it is a π complex rather than a compound with $\text{Ni}-\text{C}$ σ bonds (99).



D. Mechanism of the Formation of Cyclododecatriene

Butadiene reacts with cyclododecatriene-nickel or bis(cyclooctadiene)-nickel at 20° C, replacing the olefinic ligands and forming a new molecule of cyclododecatriene (99). In this reaction "atomic" nickel must be the catalyst, as it is in some reactions of bis(acrylonitrile)-nickel. Most of the catalytically formed cyclododecatriene has the *trans-trans-cis* configuration, but, small amounts of the *trans-cis-cis* isomer have also been detected. When the reaction between (LIV) and butadiene was carried out at -40° C. Wilke *et al.* were able to isolate an intermediate (LVI) the nature of which was of great importance in elucidating reaction mechanism. Complex (LVI) is actually a bis(π -allyl)-nickel type of compound involving a twelve-carbon-atom chain, formed by condensation of three molecules of butadiene. Allyl

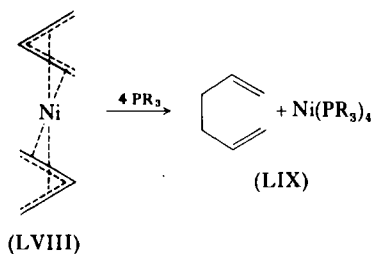


groups at the ends of the chain are bonded to the nickel atom. Upon heating, (LVI) decomposes into nickel and cyclododecatriene, but on hydrogenation *n*-dodecane is obtained (Eq. 23).

The conversion of the C_{12} chain in (LVI) to cyclododecatriene can also be achieved by treating (LVI) with electron donors such as carbon monoxide, phosphines, or even butadiene. With phosphines under mild conditions the ring closure to cyclododecatriene takes place without decomposition of the complex and cyclododecatriene-nickel-phosphine adducts are isolated (99). With carbon monoxide at -60°C (LVI) affords a vinylcycloundecadienone (LVII) (99).

E. Bis(π -allyl)-nickel

The presence of a bis(π -allyl) system in (LVI) suggested the existence of a bis(π -allyl)-nickel. Previously Fischer and Bürger had prepared a dimeric π -allylnickel bromide (102) (see Section IV, A). Wilke and Hermann obtained the desired compound by treating ethereal allylmagnesium bromide with anhydrous nickel(II) bromide (99, 103). Bis(π -allyl)-nickel (LVIII) is volatile in ether and crystallizes below 1°C into long yellow



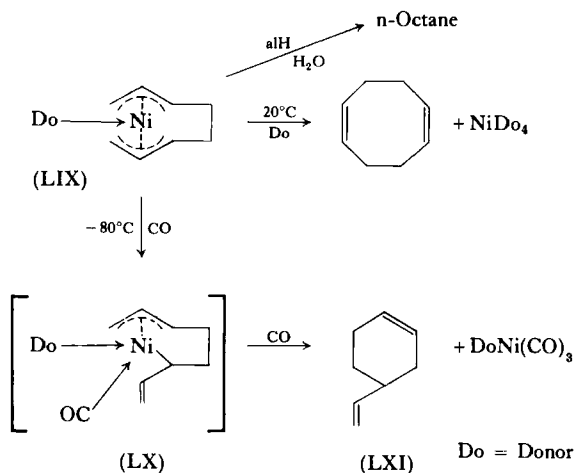
needles. Although pyrophoric, its solutions in ether are not affected by deoxygenated water, in accord with its nonclassical π -complex structure. The structure of bis(methallyl)-nickel has been determined by Dietrich and Uttech (103a). The crystals are monoclinic with $a = 6.07$, $b = 13.5$, and $c = 5.86 \text{ \AA}$. The space group is $C_{2h}^5 - P(2_1/c)$ with two molecules per unit cell. The nickel atom is situated in a center of symmetry and a two-dimensional projection indicates an "anti-sandwich" structure. With molecular hydrogen, propane and nickel are formed, and with phosphines the two allyl radicals combine to form diallyl (Eq. 24).

The insertion of carbon monoxide has not yet been achieved. Bis(π -allyl)-nickel reacts with butadiene to form cyclododecatriene. The allylic groups may also be displaced by cycloocta-1,5-diene or cyclooctatetraene. Wilke regards (LVIII) as formally a complex of Ni(II), assuming that during the catalysis there is a constant and reversible change in the formal oxidation

state of the nickel atom (99). This postulate, however, may lead to unnecessary complications. It must be stressed that the frequently exercised assignment of formal oxidation numbers to metal atoms in predominantly covalent metal-organic complexes should not be treated too seriously. Bis(π -allyl)-nickel is best regarded as a Ni(0) complex, as follows from its physical properties (volatility, etc.) than as a Ni(II) derivative. All that distinguishes it, for instance, from bis(cyclooctadiene)-nickel, is that its ligands are radicals rather than normal olefins. The driving force for the electronic and the molecular rearrangements which occur during the various catalytic processes is the tendency of the complex system to achieve greater orbital stabilization.

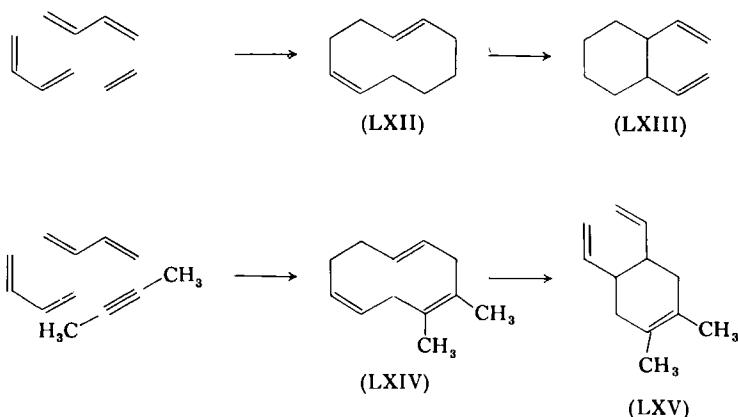
F. Catalytic Formation of Cycloocta-1,5-diene

No cyclododecatriene is obtained if reaction of butadiene with nickel-olefin complexes is conducted in the presence of donors, e.g. triphenylphosphine (99). It was mentioned previously (Section VIII, B) that triphenylphosphine stabilizes the catalytically active atomic nickel. Coordination with the electron pair of the donor in this case also has an inhibiting effect, and only cycloocta-1,5-diene is formed. In practice, the complex $\text{Ni} \cdot 4\text{P}(\text{C}_6\text{H}_5)_3$ is used, which can be made by treating bis(π -allyl)-nickel with triphenylphosphine (99, 103) (Eq. 24). This complex easily releases triphenylphosphine. In the presence of butadiene evidently three molecules are displaced by two of the diene. The activity and lifetime of the catalyst are exceptional. It is possible to convert 800–900 gm of butadiene to cyclooctadiene of 95% purity, at 80° C and atmospheric pressure, per hour and gram of nickel in the catalyst. By analogy with the mechanism of cyclododecatriene formation it was assumed that the initial complex should contain two butadiene molecules which would at first combine to give an open-chain C_8 -bis(allyl) system (LIX). This intermediate was isolated by using a suitable phosphine as an additional donor. Complex (LIX), when hydrogenated at low temperature, yields over 80% of *n*-octane. Ring closure is achieved by warming it up to 20° C and displacing the cyclooctadiene with a donor molecule, e.g., triphenylphosphine. The total π -electron energy of two butadiene molecules is $E = 2(4\alpha + 2(5)^{1/2}\beta)$. The value for the energy of two butadienes in the allylic biradical form $\text{CH}_2\cdots\text{CH}\cdots\text{CH}-\text{CH}_2$ would be $E = 2(4\alpha + 2(2)^{1/2}\beta)$, using simple Hückel theory. The energy difference between the two pairs of molecules



is 3,287 β and could be offset by forming a new C—C bond and allowing the terminal allyl systems to interact with the nickel orbitals. Although vinylcyclohexene (LXI) is the major product of the noncatalytic thermal dimerization, it may also be formed catalytically. If (LIX) at -80°C is treated with carbon monoxide, one π -allyl group is displaced in part by the free electron pair of the carbon monoxide molecule (LX). Further reaction with carbon monoxide then produces vinylcyclohexene in 80% yield (99).

Butadiene may also be co-cyclized with ethylene, forming cyclodeca-1,5-diene (LXII). With 2-butyne, 1,2-dimethylcyclodeca-1,4,8-triene (LXIV)

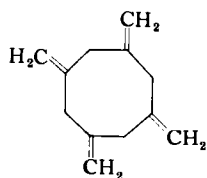


is obtained. Both products when heated undergo Cope rearrangements to (LXIII) and (LXV), respectively (99).

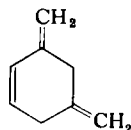
X

CYCLOPOLYMERIZATION OF ALLENE

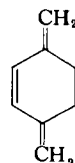
Benson and Lindsey (104) were able to cyclopolymerize allene using phosphine-nickel carbonyl complexes as catalysts. They obtained a mixture of 1,2,4- and 1,3,5-trimethylenecyclohexane, and a remarkably stable tetramer, 1,3,5,7-tetramethylenecyclooctane, (LXVI).



(LXVI)



(LXVII)



(LXVIII)

Compound (LXVI) is particularly interesting as it undergoes a 1,7 addition with tetracyanoethylene. This transannular addition is possible since the opposite pairs of double bonds in (LXVI) parallel each other at a distance of only about 2.7 Å, which must lead to appreciable π -orbital interaction (105). In the presence of acetylene, with $\text{Ni}(\text{CO})_2 \cdot 2\text{P}(\text{OC}_6\text{H}_5)_3$ as the catalyst, a co-cyclopolymerization of allene to 3,5- and 3,6-dimethylenecyclohexene (LXVII) and (LXVIII), respectively, is possible (106). With nickel acetylacetonate as catalyst, (LXVII) and 3,5,7-trimethylenecyclooctene (LXVIII) are produced in 45% and 5% yield respectively. (106). This reaction makes *exo*-methylene cyclic compounds which are unsaturated easily accessible. The chemistry of (LXVII) has been studied in some detail (107).

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The Strengths of Metal-to-Carbon Bonds

H. A. SKINNER

Chemistry Department, University of Manchester,
Manchester, England

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I

INTRODUCTION

Reliable information on the strengths of metal-to-carbon bonds is still meager, despite notable additions made within the past decade. This unsatisfactory state of affairs has been caused by the diffidence of thermochemists to tackle organometallic compounds until recently, and by failings of conventional thermochemical techniques when applied to this class of compound. In 1940, for instance, the published heat of formation data on organometallic compounds, apart from a number of metallic salts of acetic, formic, and oxalic acid, were limited to the following items:

(i) $(\text{CH}_3)_2\text{Hg}$ and $(\text{C}_2\text{H}_5)_2\text{Hg}$, by Berthelot (10) in 1899; $(\text{C}_3\text{H}_7)_2\text{Hg}$, $(i\text{-C}_3\text{H}_7)_2\text{Hg}$, $(\text{C}_4\text{H}_9)_2\text{Hg}$, $(i\text{-C}_4\text{H}_9)_2\text{Hg}$, and $(i\text{-C}_5\text{H}_{11})_2\text{Hg}$, by Jones *et al.* (87) in 1935;

(ii) $(\text{C}_2\text{H}_5)_4\text{Sn}$, $(\text{C}_3\text{H}_7)_4\text{Sn}$, $(\text{C}_4\text{H}_9)_4\text{Sn}$, and $(\text{C}_5\text{H}_{11})_4\text{Sn}$, by Jones *et al.* (87) in 1935;

- (iii) $(\text{C}_2\text{H}_5)_2\text{Zn}$, by Guntz (72) in 1887;
- (iv) CSe_2 , $(\text{C}_2\text{H}_5)_2\text{Se}$, and $(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2\text{Se}$, by Merten and Schlüter (119) in 1936;
- (v) $\text{Fe}(\text{CO})_5$, by Mittasch (120) in 1928, and by Roth (144) in 1929;
- (vi) calcium and magnesium cyanamides, by Franck and Hochwald (57) in 1925;
- (vii) a number of metal cyanides, including those of calcium and barium (56);
- (viii) $(\text{C}_2\text{H}_5)_3\text{P}$, $(\text{C}_6\text{H}_5\text{NH})_3\text{PO}$, and $(\text{CH}_3\text{C}_6\text{H}_4\text{NH})_3\text{PO}$, by Lemoult (100) in 1909.

Many of these early data are now known to be inaccurate, e.g., in the case of dimethylmercury and diethylmercury, Berthelot's values are in error by from 15–20 kcal/mole, and the errors in Jones' values for the tetraalkyls of tin range from 10 to 30 kcal/mole. It is relevant to recollect that the extensive list of bond energy values published by Pauling (126) in 1939 did not contain a single metal-carbon entry, unless one includes Si—C in this category.

Heats of formation have since been reported for some 150 or more organometallic compounds, but several of these are of doubtful reliability. However, the development of rotating-bomb calorimetry and the application of novel reaction calorimetric techniques have provided more effective means than hitherto for investigating the thermochemistry of organometallic compounds, making it almost certain that the present lack of reliable data will be short-lived.

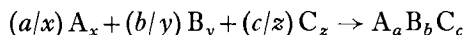
II

DEFINITIONS AND SYMBOLS

In discussing the bond energy property, it is necessary at the outset to distinguish between *bond energy term values* and *bond dissociation energies*. The distinction between these may be brought out by reference to methane as an example: Here, the bond energy term, $\bar{E}(\text{C—H})$, is measured by the *average* contribution of each C—H bond to the total heat of atomization, ΔH_a° , of the molecule and given by $\bar{E}(\text{C—H}) = \frac{1}{4}\Delta H_a^\circ$, whereas the bond dissociation energy, $D(\text{CH}_3\text{—H})$, is the *actual* heat required to rupture a C—H bond in the process

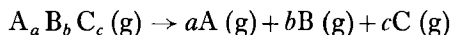


E values are derived from heats of formation, ΔH_f° , which are usually obtained by calorimetric measurements made at, or near to room temperature. Heat of formation data are therefore nowadays referred to 25°C , which has been adopted as the "standard" for thermochemical purposes. The standard heat of formation of a compound $A_aB_bC_c$ is defined as the change in heat content for the reaction in which the compound is synthesized from its constituent elements,



for reaction occurring isothermally at 25°C (298.15°K), and the elements A_x , B_y , C_z , being in their standard thermodynamic states. Should the product $A_aB_bC_c$ be a solid or a liquid at 25°C , its standard heat of formation, $\Delta H_f^\circ_{298.15^\circ\text{K}}$, includes the intermolecular binding energy of the condensed state: The latter is irrelevant to bond energy considerations. The required quantity is that relating to the product in the (hypothetical) ideal gas state, and is obtained from the measured ΔH_f° on making allowance for the heat of vaporization, ΔH_v° , (or of sublimation, ΔH_s°) to the ideal gaseous state at 25°C .

Provided $\Delta H_f^\circ(A_aB_bC_c, g)$ has been determined, the heat of the atomization process



is readily derived,

$$\Delta H_a^\circ_{298.15^\circ\text{K}} = a\Delta H_f^\circ(A, g) + b\Delta H_f^\circ(B, g) + c\Delta H_f^\circ(C, g) - \Delta H_f^\circ(A_aB_bC_c, g) \quad (1)$$

and reliable values are available for the heats of atomization (i.e., $\Delta H_f^\circ(A, g)$, etc.) of most of the common elements. These are listed in Table I, and taken mainly from recent compilations by Brewer (16), Kondratiev (91), and the JANAF¹ Thermochemical Tables (166).

The C—H bond energy term value in CH_4 is uniquely determined by dividing the total heat of atomization equally between the four bonds, i.e.,

$$E(\text{C—H}) = \frac{1}{4}\Delta H_a^\circ = 397.16/4 = 99.29 \text{ kcal/mole}$$

In general, however, bond energy terms cannot be obtained unambiguously; in ethane, for instance, the problem is to apportion the total heat of atomization (674.58 kcal/mole) between six C—H bonds and one C—C bond, and the best way of doing this is still in dispute. If one presumes that $E(\text{C—H})$ is constant in paraffins, then $E(\text{C—C})$ in ethane is uniquely determined at

¹ Joint Army, Navy, Air Force (JANAF) Thermochemical Tables.

TABLE I
HEATS OF FORMATION OF ATOMS AT 25°C

Atom	ΔH_f (g) (kcal/gm atom)	Reference	Atom	ΔH_f (g) (kcal/gm atom)	Reference
H	52.10 ± 0.06		Rb	19.5 ± 1	
Li	38.4 ± 0.4		Sr	39.1 ± 1	
Be	78.25 ± 0.5		Y	98 ± 2	
B	132 ± 5	(125, 174)	Zr	145.4 ± 0.4	
C	170.9 ± 0.45		Nb	173 ± 2	
N	113.0		Mo	157.7	
O	59.56 ± 0.03		Ru	153 ± 2	
F	18.86 ± 0.2		Rh	133 ± 1	
Na	25.8 ± 0.1		Pd	91 ± 1	
Mg	35.1 ± 0.1	(159)	Ag	68.4	
Al	78.0 ± 0.4		Cd	26.75 ± 0.2	
Si	108.4 ± 3	(38)	In	58 ± 2	
P	75.5	(77)	Sn	72.0 ± 2	
S	65.65 ± 0.6		Sb	63 ± 2	
Cl	28.92 ± 0.03		Te	46 ± 2	
K	21.3 ± 0.2		I	25.54 ± 0.01	
Ca	42.81 ± 0.02	(159)	Cs	18.7 ± 0.3	
Sc	91.2 ± 0.3	(92)	Ba	42.5	
Ti	112.5		Hf	148.0	(7)
V	123		Ta	186.8 ± 1	
Cr	95 ± 1		W	201.8 ± 2	
Mn	66.7		Re	187 ± 2	
Fe	99.5 ± 1		Os	187 ± 2	
Co	101.6		Ir	159 ± 2	
Ni	102.8		Pt	135.2 ± 1	
Cu	81.1		Au	88.3 ± 0.9	(81)
Zn	31.2 ± 0.5		Hg	14.65 ± 0.02	
Ga	69.0		Tl	43.0 ± 1	
Ge	90.2 ± 3		Pb	46.75 ± 0.13	
As	69 ± 3		Bi	49.5 ± 1	
Se	49.4 ± 1		U	115 ± 3	(138)
Br	26.74 ± 0.07		Th	136.6	

78.84 kcal/mole. But these values for $\bar{E}(\text{C—H})$ and $\bar{E}(\text{C—C})$, when substituted into the equation

$$\Delta H_a^\circ(\text{C}_n\text{H}_{2n+2}) = (2n+2)\bar{E}(\text{C—H}) + (n-1)\bar{E}(\text{C—C}) \quad (2)$$

fail to reproduce satisfactorily the experimental ΔH_a° values for $n > 2$; nor for that matter does any other choice of term values. Indeed, it is now clear

that Eq. (2) (which derives from the simple model of constant, transferable, and additive bond energy terms), is unacceptable.

Considerable improvement is achieved by replacing the Fajans energy model by one in which the total energy is written as the sum of bond energy terms *plus* the sum of interaction energies between *adjacent* bonds. Applied to paraffins, this model leads to equations which can be expressed, either in the form used by Laidler (94), or in the form used by Allen (1):

Laidler

$$\Delta H_a^\circ(\text{C}_n\text{H}_{2n+2}) = (n-1)E_{\text{CC}} + n_p E_{\text{CH}}(\text{p}) + n_s E_{\text{CH}}(\text{s}) + n_t E_{\text{CH}}(\text{t}) \quad (3)$$

where n_p , n_s , and n_t are the numbers of primary, secondary, and tertiary CH bonds in the molecule, and $E_{\text{CH}}(\text{p})$, $E_{\text{CH}}(\text{s})$, and $E_{\text{CH}}(\text{t})$ their respective term values; and

Allen

$$\Delta H_a^\circ(\text{C}_n\text{H}_{2n+2}) = (n-1)B_{\text{CC}} + (2n+2)B_{\text{CH}} + b_3\Gamma_{\text{CCC}} + c_4\Delta_{\text{CCC}} \quad (4)$$

where B_{CC} and B_{CH} are "effective" term values, Γ_{CCC} is the interaction energy associated with the grouping C—C—C and b_3 the number of such groupings; Δ_{CCC} is the interaction due to the grouping of three C atoms round another C atom, and c_4 is the number of such C_3 trios in the molecule.

Other modifications of the original Fajans model have been proposed, and are discussed elsewhere (155). For present purposes, we restrict ourselves to the Allen scheme, and have used this to evaluate the various parameters (B , Γ , Δ) for selected metal-carbon bonds in Section V.

Bond energy term values do not bear a simple relation to bond dissociation energies, and are not necessarily numerically identical with them; on the contrary, the two measures often differ by substantial amounts. The widespread acceptance of \bar{E} values as an index of bond strength continues nonetheless, largely as a matter of expediency due to the lack of more direct information.

The principal experimental methods for measuring bond dissociation energies in polyatomic molecules have been described in detail by Cottrell (35). Two methods in particular have proved fruitful in recent years, namely the "toluene carrier gas" technique introduced by Szwarc (167) to investigate the unimolecular kinetics of pyrolytic decomposition reactions, and the "electron impact" method, as applied by Stevenson (165) and widely used since by several investigators. These methods do not usually give very sharp D values, and the number of well-authenticated (± 2

kcal/mole) bond dissociation energies in polyatomics remains disappointingly small. Included among them, however, are a few C—H bond dissociation energies in simple hydrocarbons, from which the heats of formation of a number of organic free radicals have been derived. These are listed in Table II.

TABLE II
HEATS OF FORMATION OF FREE RADICALS

Radical ^b	ΔH_f° (g) (kcal/mole)	Reference
Me	33 \pm 1	(44, 90)
Et	25.5 \pm 2	(41, 74, 90)
Pr	20.5 \pm 2	(41)
Bu	15.5 \pm 2 ^a	—
<i>i</i> -Pr	17 \pm 2	(151)
<i>t</i> -Bu	5 \pm 2	(151)
Ph	72 \pm 2	(45)
Bz	42 \pm 3	(37)
Vn	65 \pm 3	(73)
cyclo-C ₅ H ₅	45.4 \pm 10	(139)
—CN	109	(9)

^a Assuming $D(\text{Bu—H}) = D(\text{Pr—H})$.

^b Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; *i*-Pr, isopropyl; *t*-Bu, *tert*-butyl; Ph, phenyl; Bz, benzyl; Vn, vinyl.

ΔH_f° values of free radicals can be used to derive *mean* dissociation energies of metal–carbon bonds in metallic alkyls and related compounds. Thus, if both ΔH_f° (MR_{*n*}, g) and ΔH_f° (R, g) are known, the heat of the disruption process



in which *all* the metal–carbon bonds are broken, is given by

$$\Delta H^\circ = \Delta H_f^\circ (\text{M}, \text{g}) + n\Delta H_f^\circ (\text{R}, \text{g}) - \Delta H_f^\circ (\text{MR}_n, \text{g}) \quad (5)$$

and the *mean* bond dissociation energy, $\bar{D}(\text{M—R})$ is $\Delta H^\circ/n$. In general, \bar{D} values will differ from \bar{E} values, and from actual metal–carbon dissociation energies, $D(\text{R}_{n-1}\text{M—R})$. The latter have received only scant attention and very few measured values have been reported. They are discussed in Section VII.

Although not specifically stated in Eq. (1), the heats of formation, ΔH_f° (A), ΔH_f° (B), etc., refer to the *ground states* of the atoms A, B, etc. \bar{E} values derived from ΔH_a° data are thus measured with respect to ground states of the atoms involved. This procedure has been questioned since atoms in molecules often exhibit a valence different from that in their ground states. The reasonable proposal has been made that bond energy terms should be referred to the *valence states* of the bonded atoms, and although this raises new difficulties (155, 175), it is useful to examine these so-called "*intrinsic*" bond energy terms, or \bar{E}^* values, in certain cases.

III

HEATS OF FORMATION OF ORGANOMETALLIC COMPOUNDS—EXPERIMENTAL METHODS

The experimental determination of the heat of formation of an organic compound will usually require the investigator to measure the heat of combustion of the compound in a suitable calorimeter. If the compound is a gas, or volatile liquid at room temperature, the flame calorimeter (141) offers itself as a suitable instrument; but for most liquid or solid compounds, the bomb calorimeter is the obvious choice. There are, however, decided limitations to the usefulness of conventional calorimeters when organometallic compounds are under investigation.

The difficulties stem from the fact that the metallic component rarely burns completely, so that the solid inorganic residue resulting from combustion consists of a *mixture* of products which may be complex. In this event, the measured combustion heat refers to a process which can only be properly defined if the products of combustion are accurately analyzed. The problem is not merely analytical, because the solid products are deposited in the crucible, and on the walls of the bomb, and the composition of the deposit varies from one part of the bomb to another. A striking example, quoted by Good and Scott (65), is provided by Knowlton's study of the combustion of tetraethyllead in a conventional bomb calorimeter; the solid product was found to contain PbO, PbO₂, PbCO₃, and Pb(NO₃)₂ admixed with unburned Pb, but the interpretation of the measured heat of combustion with respect to these products led to a value for the heat of formation of tetraethyllead which was in error by no less than 40 kcal/mole! This is, perhaps, an extreme example, but the fact remains that conventional

bomb methods for organometallic compounds cannot always be expected to achieve high accuracy. Fortunately, the development of the technique of *rotating-bomb* calorimetry has provided a means of overcoming the deficiencies of the conventional apparatus, and the way is now open for accurate measurements of the heats of combustion of some, if not most, organometallic compounds.

A. Rotating-Bomb Methods

Rotating-bomb calorimeters and their operation have been described in detail in Vols. 1 and 2 of "Experimental Thermochemistry" (140, 152). In this type of calorimeter, the bomb is charged prior to starting the experiment with an adequate volume of a chosen solvent *capable of dissolving the solid combustion products*. After firing the sample, the bomb is set in motion by imparting end-over-end and axial rotations to it, thereby bringing the solvent into intimate contact with the solid products, wherever they may be placed in the bomb. A solution of uniform concentration, capable of precise thermodynamic definition, is the final product. The rotating-bomb calorimeter thus combines in one instrument the functions of a combustion bomb calorimeter and a solution reaction calorimeter.

The method has been applied to six organometallic compounds only, namely, tetramethyllead (66), tetraethyllead and lead oxalate (148), dimanganese decacarbonyl (62), hexamethyldisiloxane (63), and triphenylarsine (123). Nevertheless, these few examples clearly reveal the power of the method and can leave no doubt of its future potential.

For the study of organolead compounds, the solvent used was a solution of nitric acid, containing a little arsenious acid. The nitric acid dissolved all the solid lead compounds in the 2+ oxidation state (PbO , PbCO_3), and also was able, in the presence of oxygen under pressure, to dissolve the finely divided metallic lead. The arsenious acid, in the presence of nitric acid, reduced lead compounds in higher oxidation states (PbO_2) to Pb^{2+} ion in solution. The solid combustion product was thus entirely converted into a solution of lead nitrate. For the study of dimanganese decacarbonyl, the solvent used was a mixture of nitric acid and hydrogen peroxide, the final product being a solution of $\text{Mn}(\text{NO}_3)_2$. In this case, it was found necessary to use a lower O_2 pressure than normal in the bomb in order to obtain the solid products in a finely divided state, so that they dissolved readily. For the investigation of hexamethyldisiloxane, the method used was to burn the

silicon compound together with benzotrifluoride. In this way, the silica formed on combustion dissolved in the aqueous hydrofluoric acid produced by combustion of the benzotrifluoride; and rotation (solvent, water) gave a uniform solution of hydrofluosilicic acid in aqueous hydrofluoric acid.

B. Reaction Calorimetric Methods

The calorimetric measurement of the heats of reactions *other than combustion* is conveniently referred to under the single heading of "reaction calorimetry." Typical reactions include hydrolysis, hydrogenation, halogenation, and thermal decomposition; calorimeters designed for the study of these and other types of reaction have been described in detail elsewhere (156).

The chemical reactivity of organometallic compounds, in particular those of the elements of Groups I, II, and III, renders them well-suited to study by reaction calorimetric methods. Examples reported include measurements of the heats of hydrolysis of alkyls of Li, Zn, Cd, and Al, the heats of hydroboration of olefins, and the heats of halogenation of alkyls of Zn, Cd, Hg, Sn, and Ga. The heat of formation data derived by use of these methods are discussed in the following Section, in which "best" ΔH_f° values are selected from the available published data on compounds containing metal-carbon bonds.

IV

SELECTED ΔH_f° VALUES OF ORGANOMETALLIC COMPOUNDS

The values discussed in this section are summarized in Table III at the end of this section. The selected values for the heats of formation are indicated by the notation (**).

Ethyllithium (crystalline)

Measurements of the heat of combustion, using a static bomb calorimeter, have been reported by Lebedev *et al.* (99). The solid product of combustion was mainly Li_2O , admixed with Li_2O_2 and Li_2CO_3 . The corrected $\Delta H_c^\circ = -416.2 \pm 1.3$ kcal/mole refers to the formation of Li_2O , CO_2 , and H_2O (liq), and corresponds to

$$\Delta H_f^\circ (\text{EtLi, c}) = -14.0 \pm 1.3 \text{ kcal/mole} \quad (**)$$

Ethyllithium (gas)

Chaiken (26) measured the vapor pressure over the temperature range 25–60° C, by an effusion method, and obtained $\Delta H_s = 27.9 \pm 0.2$ kcal/mole. Therefore,

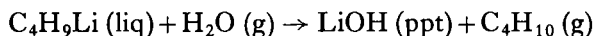
$$\Delta H_f^\circ (\text{EtLi}, g) = 13.9 \pm 1.4 \text{ kcal/mole} \quad (**)$$

However, it seems that the vapor of ethyllithium is composed mainly of polymeric species. Berkowitz *et al.* (9a) examined the saturated vapor at 80–95° C of ethyllithium by means of the mass spectroscopy and detected peaks corresponding to $\text{Li}_n\text{Et}_{n-1}^+$ for all values of n from 1 to 6 inclusive. The most abundant ions were Li_6Et_5^+ and Li_4Et_3^+ , implying that the hexamer and tetramer constitute the predominant vapor species. West and Glaze (176b), from studies of the infrared spectrum of ethyllithium as vapor at 80° C (and in solution), concluded that certain complex vibrations involving the lithium atoms are consistent only with polymer molecules. The heat of depolymerization to monomer is not yet available.

Butyllithium (liquid)

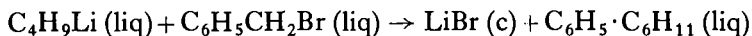
Lebedev *et al.* (99) measured the heat of combustion, $\Delta H_c^\circ = -722.8 \pm 1.7$ kcal/mole. Consequently, $\Delta H_f^\circ (\text{BuLi}, \text{liq}) = -32.0 \pm 1.7$ kcal/mole.

Fowell and Mortimer (54) measured the heat of the hydrolysis reaction



obtaining $\Delta H^\circ = -57.4 \pm 0.7$ kcal/mole. Assuming (166) that $\Delta H_f^\circ (\text{LiOH}, c) = -116.6 \pm 0.4$ kcal/mole this leads to $\Delta H_f^\circ (\text{BuLi}, \text{liq}) = -31.5 \pm 1.0$ kcal/mole, in good agreement with the combustion result.

Fowell and Mortimer also obtained $\Delta H^\circ = -80.8 \pm 2.6$ kcal/mole for the reaction



This, combined with the available values, $\Delta H_f^\circ (\text{LiBr}, c) = -83.7$ (143); $\Delta H_f^\circ (\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_{11}, \text{liq}) = -21.4 \pm 0.5$ (142); and $\Delta H_f^\circ (\text{C}_6\text{H}_5\text{CH}_2\text{Br}, \text{liq}) = 3.8 \pm 0.5$ kcal/mole (3), leads to $\Delta H_f^\circ (\text{BuLi}, \text{liq}) = -28.1 \pm 2.7$ kcal/mole.

The value derived from the hydrolysis study seems the most reliable of these determinations, and the selected "best" value is weighted by it

$$\Delta H_f^\circ (\text{BuLi}, \text{liq}) = -31.0 \pm 2 \text{ kcal/mole} \quad (**)$$

Butyllithium (gas)

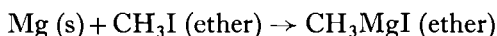
Lebedev *et al.* (99) obtained $\Delta H_v = 25.6 \pm 0.7$ kcal/mole from vapor pressure measurements over the range 60–95° C. Hence,

$$\Delta H_f^\circ (\text{BuLi, g}) = -5.4 \pm 2.2 \text{ kcal/mole} \quad (**)$$

It is not established that the vapor of *n*-butyllithium is polymeric, although one must presume that this is likely, particularly since Weiner *et al.* (176a) have shown that *tert*-butyllithium has a tetrameric structure.

Methylmagnesium Iodide (ether solution)

Carson and Skinner (23) measured the heat of solution of Mg metal in an ether solution of methyl iodide,



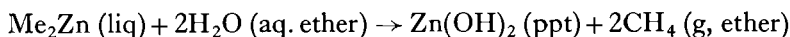
and obtained $\Delta H^\circ = -65.4 \pm 0.2$ kcal/mole. Assuming $\Delta H_f^\circ (\text{CH}_3\text{I, liq}) = -2.9 \pm 0.5$ kcal/mole (19), this leads to

$$\Delta H_f^\circ (\text{CH}_3\text{MgI, ether}) = -68.3 \pm 0.6 \text{ kcal/mole} \quad (**)$$

Dimethylzinc (liquid)

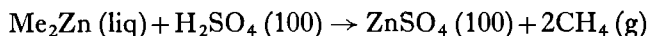
Long and Norrish (103) measured the heat of combustion, using a static bomb calorimeter. The solid products of combustion consisted mainly of ZnO, admixed with ZnCO₃ and hydrated ZnO. Combustion was usually incomplete, and traces of soot remained in the crucible. Corrections were made for soot formation, and for formation of ZnCO₃; the corrected value, $\Delta H_c^\circ = -482.8 \pm 2$ kcal/mole, relates to the formation of ZnO (c, hexagonal), CO₂, and H₂O (liq) as sole products. Accepting $\Delta H_f^\circ (\text{ZnO, c}) = -83.2 \pm 0.3$ kcal/mole (143), the derived heat of formation is $\Delta H_f^\circ (\text{Me}_2\text{Zn, liq}) = 6.5 \pm 2$ kcal/mole.

Carson *et al.* (22) measured the heat of hydrolysis in aqueous ether solution



finding $\Delta H = -59.2 \pm 0.3$ kcal/mole. Accepting $\Delta H_f^\circ [\text{Zn(OH)}_2, \text{c}] = -153.5$ kcal/mole (143), and correcting for partial solution of CH₄ in the ether solvent ($\Delta H_{\text{soln}} \sim -\frac{1}{2}$ kcal), the value $\Delta H_f^\circ (\text{Me}_2\text{Zn, liq}) = 6.1 \pm 2$ kcal/mole is derived. The uncertainty arises mainly from the ill-defined nature of precipitated Zn(OH)₂, for which a sharp ΔH_f° value is lacking (58).

Carson *et al.* also measured the heat of decomposition of Me_2Zn by dilute sulfuric acid,



leading to $\Delta H_f^\circ (\text{Me}_2\text{Zn, liq}) = 5.5 \pm 2$ kcal/mole. The uncertainty here arises from side reactions induced by the violence of the main reaction.

The good agreement between the results of these different determinations is probably fortuitous, in view of the experimental difficulties involved; the selected value is

$$\Delta H_f^\circ (\text{Me}_2\text{Zn, liq}) = 6.0 \pm 2 \text{ kcal/mole} \quad (**)$$

Dimethylzinc (gas)

From vapor pressure data given by Long and Cattanach (102), $\Delta H_v^\circ = 7.06$ kcal/mole at 25°C . Hence,

$$\Delta H_f^\circ (\text{Me}_2\text{Zn, g}) = 13.1 \pm 2 \text{ kcal/mole} \quad (**)$$

Diethylzinc (liquid)

Long and Norrish (103) reported $\Delta H_c^\circ = -805.1 \pm 4$ kcal/mole, corresponding to $\Delta H_f^\circ = 4.1 \pm 4$ kcal/mole. Lautsch *et al.* (98) have also measured the heat of combustion, finding $\Delta H_c^\circ = -802.1 \pm 3$ kcal/mole, or $\Delta H_f^\circ = 1.1 \pm 3$ kcal/mole.

Carson *et al.* measured the heat of hydrolysis in aqueous ether solution and the heat of decomposition by dilute sulfuric acid. These experiments gave $\Delta H_f^\circ = 4.6$ and 3.6 kcal/mole, respectively. In both cases the uncertainty is of the order ± 2 kcal/mole, for the same reasons as with Me_2Zn . The selected value is

$$\Delta H_f^\circ (\text{Et}_2\text{Zn, liq}) = 4.0 \pm 2 \text{ kcal/mole} \quad (**)$$

Diethylzinc (gas)

From vapor pressure data given by Jordan (88) $\Delta H_v^\circ = 8.75$ kcal/mole at 48°C , or 9.05 kcal/mole at 25°C ,

$$\Delta H_f^\circ (\text{Et}_2\text{Zn, g}) = 13.0_5 \pm 2 \text{ kcal/mole} \quad (**)$$

Dipropylzinc (liquid)

Long and Norrish (103) reported $\Delta H_c^\circ = -1112.1 \pm 6$ kcal/mole, leading to

$$\Delta H_f^\circ (\text{Pr}_2\text{Zn, liq}) = -13.6 \pm 6 \text{ kcal/mole} \quad (**)$$

Dibutylzinc (liquid)

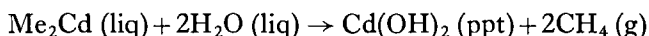
Long and Norrish obtained $\Delta H_c^\circ = -1425.6 \pm 6$ kcal/mole. Therefore,

$$\Delta H_f^\circ (\text{Bu}_2\text{Zn, liq}) = -24.9 \pm 6 \text{ kcal/mole} \quad (**)$$

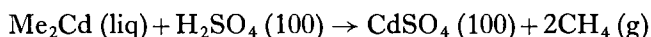
Dimethylcadmium (liquid)

Long and Norrish (103) studied the combustion of Me_2Cd using a static bomb calorimeter. The solid product of combustion contained considerable amounts of unburned Cd, and some soot, admixed with CdO . Individual combustion results showed a wide scatter, and the "corrected" value for complete combustion, $\Delta H_c^\circ = -475.4$ kcal/mole was considered uncertain to ± 3 kcal/mole. Assuming $\Delta H_f^\circ (\text{CdO, c}) = -61.2 \pm 0.2$ kcal/mole (110), the derived heat of formation is $\Delta H_f^\circ (\text{Me}_2\text{Cd, liq}) = 20.1 \pm 3$ kcal/mole.

Carson *et al.* (21) measured the heat of hydrolysis



finding $\Delta H^\circ = -48.5 \pm 0.2$ kcal/mole. Assuming $\Delta H_f^\circ [\text{Cd(OH)}_2, \text{c}] = -133.3$ kcal/mole (143), this leads to $\Delta H_f^\circ (\text{Me}_2\text{Cd, liq}) = 16.1 \pm 1$ kcal/mole, the uncertainty arising from the lack of precision in the assumed value for ΔH_f° of Cd(OH)_2 . To improve on this, measurements were made of the heat of decomposition of Me_2Cd by aqueous sulfuric acid, the products in this case being thermodynamically well-defined



From the measured heat, $\Delta H^\circ = -73.3 \pm 0.15$ kcal/mole, the value

$$\Delta H_f^\circ (\text{Me}_2\text{Cd, liq}) = 16.7 \pm 0.2 \text{ kcal/mole} \quad (**)$$

is derived, and is selected here as the best.

Dimethylcadmium (gas)

From vapor pressure measurements by Anderson and Taylor (2), $\Delta H_v^\circ = 9.53$ kcal/mole at 25°C . Hence,

$$\Delta H_f^\circ (\text{Me}_2\text{Cd, g}) = 26.2 \pm 0.3 \text{ kcal/mole} \quad (**)$$

Diethylcadmium (liquid)

Lautsch *et al.* (98) measured the heat of combustion, finding $\Delta H_c^\circ = -800.0 \pm 3$ kcal/mole; this corresponds to $\Delta H_f^\circ = 21.0 \pm 3$ kcal/mole. Few details in the investigation were given, and the result cannot be regarded as well-founded.

Carson *et al.* (22) measured the heat of decomposition of Et_2Cd by aqueous sulfuric acid, finding $\Delta H^\circ = -75.8 \pm 0.4$ kcal/mole. This leads to

$$\Delta H_f^\circ (\text{Et}_2\text{Cd, liq}) = 14.5 \pm 0.4 \text{ kcal/mole} \quad (**)$$

and is accepted as the best value.

Diethylcadmium (gas)

Vapor pressure measurements are insufficient to provide a reliable value for ΔH_v . We have estimated 11.0 ± 0.5 kcal/mole for ΔH_v at 25°C , so that

$$\Delta H_f^\circ (\text{Et}_2\text{Cd, g}) = 25.5 \pm 0.7 \text{ kcal/mole} \quad (**)$$

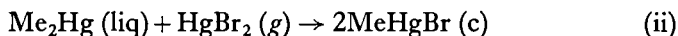
Dimethylmercury (liquid)

Carson *et al.* (18) measured the heats of combustion of Me_2Hg , Et_2Hg , and Ph_2Hg using a static bomb calorimeter. Most of the mercury did not burn, but small amounts of red HgO formed on the internal fittings and bomb walls. Traces of $\text{Hg}(\text{NO}_3)_2$ were also found. After correction for these side reactions, Carson *et al.* obtained $\Delta H_f^\circ (\text{Me}_2\text{Hg, liq}) = 14.3$ kcal/mole.

Hartley *et al.* (75) measured the heat of bromination of dimethylmercury via the reactions



and



therefore



$$\Delta H (\text{iii}) = 2\Delta H (\text{i}) - \Delta H (\text{ii})$$

Hartley *et al.* found $\Delta H (\text{iii}) = -72.15 \pm 0.6$ kcal/mole; combining this with $\Delta H_f^\circ (\text{HgBr}_2, \text{c}) = -40.64 \pm 0.24$ kcal/mole (173), and with $\Delta H_f^\circ (\text{MeBr, g}) = -8.5 \pm 0.5$ (52) yields $\Delta H_f^\circ (\text{Me}_2\text{Hg, liq}) = 14.5 \pm 1.2$ kcal/mole.

Similar measurements were made to obtain the heat of iodination of dimethylmercury. $\Delta H (\text{iii}) = -44.1 \pm 0.5$ kcal/mole. Assuming $\Delta H_f^\circ (\text{HgI}_2, \text{c}) = -25.2 \pm 0.2$ (173) and $\Delta H_f^\circ (\text{CH}_3\text{I, liq}) = -2.9 \pm 0.5$ kcal/mole (19), the value $\Delta H_f^\circ (\text{Me}_2\text{Hg, liq}) = 13.1 \pm 1.1$ kcal/mole is derived.

The selected value is the mean of those found from the halogenation and combustion studies,

$$\Delta H_f^\circ (\text{Me}_2\text{Hg, liq}) = 14.0 \pm 1 \text{ kcal/mole} \quad (**)$$

Dimethylmercury (gas)

From vapor pressure measurements over a range of temperatures, Long and Cattanach (102) obtained $\Delta H_v^\circ = 8.26$ kcal/mole at 25° C. Consequently,

$$\Delta H_f^\circ (\text{Me}_2\text{Hg, g}) = 22.3 \pm 1 \text{ kcal/mole} \quad (**)$$

Diethylmercury (liquid)

The heat of combustion, measured by Carson *et al.*, gives $\Delta H_f^\circ (\text{Et}_2\text{Hg, liq}) = 6.5$ kcal/mole.

The heat of bromination of Et_2Hg measured by Hartley *et al.* (76), ΔH (iii) = -91.25 ± 0.3 kcal/mole, combined with the value (70), $\Delta H_f^\circ (\text{C}_2\text{H}_5\text{Br, liq}) = -22.1 \pm 0.5$ kcal/mole, leads to $\Delta H_f^\circ (\text{Et}_2\text{Hg, liq}) = 6.4 \pm 1.0$ kcal/mole in close agreement with the value derived from combustion studies. The selected value is

$$\Delta H_f^\circ (\text{Et}_2\text{Hg, liq}) = 6.5 \pm 1 \text{ kcal/mole} \quad (**)$$

Diethylmercury (gas)

Vapor pressure measurements over the range 64–80° C (88) gave $\Delta H_v^\circ = 10.1$ kcal/mole at 72° C, corresponding to 10.7 kcal/mole at 25° C. Hence,

$$\Delta H_f^\circ (\text{Et}_2\text{Hg, g}) = 17.2 \pm \text{kcal/mole} \quad (**)$$

Di-n-propylmercury (liquid)

Mortimer *et al.* (122) measured the heat of bromination of Pr_2Hg , finding ΔH (iii) = -91.8 ± 0.5 kcal/mole. Bjellerup (14) has measured the heat of formation of propyl bromide by combustion calorimetry, but his value seems inconsistent relative to available values for EtBr and $n\text{-BuBr}$ (154); we prefer to accept an estimated value, $\Delta H_f^\circ (\text{PrBr, g}) = -21.1 \pm 1$ kcal/mole, corresponding to $\Delta H_f^\circ (\text{PrBr, liq}) = -28.85$ kcal/mole. Using this,

$$\Delta H_f^\circ (\text{Pr}_2\text{Hg, liq}) = -6.5 \pm 2 \text{ kcal/mole} \quad (**)$$

is derived.

Di-n-propylmercury (gas)

Tees (169) measured the vapor pressure over the range 35–71° C, finding $\Delta H_v^\circ = 12.8 \pm 0.3$ kcal/mole at 53° C, or 13.15 at 25° C. Hence,

$$\Delta H_f^\circ (\text{Pr}_2\text{Hg, g}) = 6.6_5 \pm 2.1 \text{ kcal/mole} \quad (**)$$

Diisopropylmercury (liquid)

Mortimer *et al.* (122) measured the heat of bromination of diisopropylmercury, finding ΔH (iii) = -98.92 ± 0.5 kcal/mole. Combination of this with Bjellerup's (14) ΔH_f° (*i*-PrBr, liq) = -30.85 ± 0.4 kcal/mole yields

$$\Delta H_f^\circ (\textit{i}\text{-Pr}_2\text{Hg, liq}) = -3.4 \pm 1 \text{ kcal/mole} \quad (**)$$

Diisopropylmercury (gas)

Tees (169) measured the vapor pressure over the range 25–63°C as $\Delta H_v = 12.5 \pm 0.4$ kcal/mole at 44°C, or 12.75 ± 0.4 kcal/mole at 25°C. Consequently,

$$\Delta H_f^\circ (\textit{i}\text{-Pr}_2\text{Hg, g}) = 9.3_5 \pm 1.1 \text{ kcal/mole} \quad (**)$$

Diphenylmercury (crystalline)

Fairbrother and Skinner (42) measured the heat of combustion in a static bomb calorimeter, obtaining $\Delta H_c^\circ = -1537.1 \pm 1.8$ kcal/mole, leading to ΔH_f° (Ph₂Hg, c) = 66.9 ± 2 kcal/mole. A similar study by Wilmshurst (181) gave $\Delta H_f^\circ = 68.3 \pm 1.5$ kcal/mole.

Chernick *et al.* (28) measured the heat of reaction of Ph₂Hg with HCl, and with HgCl₂, from which they derived ΔH_f° (Ph₂Hg, c) = 65.4 ± 2 kcal/mole.

From the measured heat of reaction of Ph₂Hg with iodine, and with HgI₂ (28, 76), and Smith's value (160) for ΔH_f° (PhI, liq) = 27.36 ± 0.5 kcal/mole, the value ΔH_f° (Ph₂Hg, c) = 66.7 ± 1 kcal/mole is derived.

The value selected here is the mean of the above,

$$\Delta H_f^\circ (\text{Ph}_2\text{Hg, c}) = 66.8 \pm 1.5 \text{ kcal/mole} \quad (**)$$

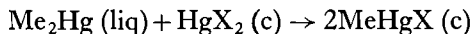
Diphenylmercury (gas)

Carson *et al.* (24) have measured the vapor pressure of diphenylmercury over a short temperature range near to 25°C by using the Knudsen effusion method on a sample of Ph₂Hg labeled with the radioisotope Hg²⁰³. They obtained $\Delta H_s^\circ = 26.95 \pm 0.2$ kcal/mole. Therefore,

$$\Delta H_f^\circ (\text{Ph}_2\text{Hg, g}) = 93.7_5 \pm 1.6 \text{ kcal/mole} \quad (**)$$

Methylmercuric Halides

Hartley *et al.* (75) measured the heats of the redistribution reactions (in alcohol solution)



(where X = Cl, Br, I). Charnley and Skinner (27) obtained the heats of sublimation of the crystalline methylmercuric halides from vapor pressure measurements, using a quartz fiber vibration gauge. These studies led to the tabulated results (kcal/mole).

	ΔH_f° (c)	ΔH_s	ΔH_f° (g)
MeHgCl	-27.8 ± 0.6	15.5 ± 0.4	-12.3 ± 0.7
MeHgBr	-20.6 ± 0.6	16.2 ± 0.4	-4.4 ± 0.7
MeHgI	$-10.3_5 \pm 0.6$	15.6 ± 0.4	5.25 ± 0.7

Ethylmercuric Halides

Hartley *et al.* (76) measured the heats of redistribution of Et_2Hg with mercuric halides; Charnley and Skinner (27) measured the heats of sublimation of the ethylmercuric halides.

	ΔH_f° (c)	ΔH_s	ΔH_f° (g)
EtHgCl	-34.0 ± 0.7	18.2 ± 0.7	-15.8 ± 1.0
EtHgBr	$-25.9_5 \pm 0.7$	18.3 ± 0.7	$-7.6_5 \pm 1.0$
EtHgI	$-15.9_5 \pm 0.8$	19.0 ± 0.7	$3.0_5 \pm 1.1$

Propyl and Isopropylmercuric Halides

Mortimer *et al.* (122) measured the heats of redistribution of propyl and isopropylmercury with mercuric halides, leading to the tabulated values.

	ΔH_f° (kcal/mole)		ΔH_f°
HgPrCl (c)	-40.6 ± 1.0	Hg <i>i</i> -PrCl (c)	-39.7 ± 0.6
HgPrBr (c)	-32.7 ± 1.0	Hg <i>i</i> -PrBr (c)	-32.6 ± 0.6
HgPrI (c)	-22.2 ± 1.0	Hg <i>i</i> -PrI (c)	-22.1 ± 0.6

Phenylmercuric Halides

Chernick *et al.* (28) measured the heat of reaction of diphenylmercury with HCl, and also with mercuric chloride. From these studies, ΔH_f° (PhHgCl, c) = 0.4 ± 1.6 kcal/mole and -0.3 ± 0.8 kcal/mole, respectively. The selected value is the mean

$$\Delta H_f^\circ (\text{PhHgCl, c}) = 0.0_5 \pm 1.2 \text{ kcal/mole} \quad (**)$$

The heat of sublimation of PhHgCl has been obtained from vapor pressure measurements using the mass spectrometer; $\Delta H_s = 24.5 \pm 1$ kcal/mole.

$$\Delta H_f^\circ (\text{PhHgCl, g}) = 24.5_5 \pm 1.5 \text{ kcal/mole} \quad (**)$$

From measurements of the heats of redistribution with HgBr₂ and HgI₂ (28, 76), ΔH_f° (PhHgBr, c) = 7.8 ± 1.2 kcal/mole; ΔH_f° (PhHgI, c) = 17.6 ± 1.2 kcal/mole.

Mercuric cyanide (gas)

Galvin and Pritchard (60) obtained $\Delta H_s = 26 \pm 1$ kcal/mole from transpiration measurements on Hg(CN)₂ over the range 200–300° C. Accepting this value at 25° C, and combining with ΔH_f° [Hg(CN)₂, c] = 62.5 kcal/mole (143), gives

$$\Delta H_f^\circ [\text{Hg(CN)}_2, \text{g}] = 88.5 \pm 2 \text{ kcal/mole} \quad (**)$$

Trimethylborane (liquid)

The combustion in a static bomb calorimeter has been studied by Long and Norrish (103) and more recently by Johnson *et al.* (86). The latter found that most of the boron burns to form boric oxide, which becomes hydrated for the most part to boric acid, and that small amounts of an insoluble darkly-colored material are also formed. This was shown to contain B₄C, and may also have contained elemental boron and soot. For the idealized combustion process



Johnson *et al.* concluded $\Delta H_c^\circ = -714.5 \pm 5.4$ kcal/mole, the large uncertainty reflecting the difficulty of defining the bomb combustion process in detail. Using the value ΔH_f° (boric acid, c) = -261.47 ± 0.20 kcal/mole recently reported by Good *et al.* (64), this determination yields

$$\Delta H_f^\circ (\text{Me}_3\text{B, liq}) = -34.1 \pm 5.5 \text{ kcal/mole} \quad (**)$$

Trimethylborane (gas)

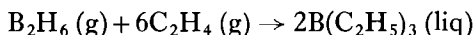
Furukawa and Park (59) have reported $\Delta H_v = 4.83$ kcal/mole at 25° C. Therefore,

$$\Delta H_f^\circ (\text{Me}_3\text{B}, \text{g}) = -29.2_5 \pm 5.5 \text{ kcal/mole} \quad (**)$$

Triethylborane (liquid)

Johnson *et al.* (86) measured the heat of combustion, $\Delta H_c^\circ = -1189.2 \pm 3.6$ kcal/mole. Therefore, $\Delta H_f^\circ (\text{Et}_3\text{B}, \text{liq}) = -46.5 \pm 3.7$ kcal/mole.

Pope and Skinner (129) measured the heat of addition of diborane to ethylene in "monoglyme" solvent, finding $\Delta H^\circ = -172.5 \pm 2$ kcal/mole for the "idealized" reaction



The heat of hydrolysis of diborane has been measured by Gunn and Green (71) and by Prosen *et al.* (135); the mean of the two determinations is $\Delta H_{\text{hyd}} = -111.84 \pm 0.5$ kcal/mole, which, in conjunction with Good's value (64) for the heat of formation of boric acid yields $\Delta H_f^\circ (\text{B}_2\text{H}_6, \text{g}) = 9.1_5 \pm 0.5$ kcal/mole. Giving slightly greater weight to Gunn's heat of hydrolysis value, we adopt $\Delta H_f^\circ (\text{B}_2\text{H}_6, \text{g}) = 9.2 \pm 0.5$ kcal/mole, yielding $\Delta H_f^\circ (\text{Et}_3\text{B}, \text{liq}) = -44.1_5 \pm 1.2$ kcal/mole. The selected value is the mean of the combustion and reaction calorimetric determinations,

$$\Delta H_f^\circ (\text{Et}_3\text{B}, \text{liq}) = -45.3_3 \pm 2.5 \text{ kcal/mole} \quad (**)$$

Triethylborane (gas)

Furukawa and Park (59) have reported $\Delta H_v = 8.8 \pm 0.2$ kcal/mole at 25° C. Consequently,

$$\Delta H_f^\circ (\text{Et}_3\text{B}, \text{g}) = -36.5_3 \pm 2.5 \text{ kcal/mole} \quad (**)$$

Tributylborane (liquid)

Johnson *et al.* (86) measured the heat of combustion, $\Delta H_c^\circ = -2127.4 \pm 2.4$ kcal/mole, leading to

$$\Delta H_f^\circ (\text{Bu}_3\text{B}, \text{liq}) = -82.5 \pm 2.5 \text{ kcal/mole} \quad (**)$$

Tributylborane (gas)

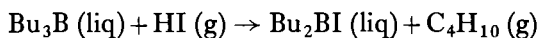
Vapor pressure measurements by Skinner and Tees (158) indicate $\Delta H_v = 13.8$ kcal/mole at 25° C. This value is low compared with ΔH_v for

Bu_3CH , and we prefer to select the same value, $\Delta H_v = 14.8 \pm 0.5$ kcal/mole, as for Bu_3CH ,

$$\Delta H_f^\circ (\text{Bu}_3\text{B}, \text{g}) = -67.7 \pm 2.6 \text{ kcal/mole} \quad (**)$$

Dibutylidoborane (liquid)

Skinner and Tees (158) measured the heat of the reaction



finding $\Delta H = -20.16 \pm 0.15$ kcal/mole. Accepting $\Delta H_f^\circ (\text{C}_4\text{H}_{10}, \text{g}) = -30.15$ kcal/mole, and $\Delta H_f^\circ (\text{HI}, \text{g}) = 6.20$ kcal/mole (143), this leads to

$$\Delta H_f^\circ (\text{Bu}_2\text{BI}, \text{liq}) = -66.3 \pm 2.5 \text{ kcal/mole} \quad (**)$$

Dibutylidoborane (gas)

We have estimated $\Delta H_v = 13.0 \pm 0.5$ kcal/mole, by comparison with measured ΔH_v for Bu_2BBr and Bu_2BCl ; hence

$$\Delta H_f^\circ (\text{Bu}_2\text{BI}, \text{g}) = -53.3 \pm 2.6 \text{ kcal/mole} \quad (**)$$

Dibutylbromoborane (liquid)

Skinner and Tees measured the heat of reaction of Bu_3B with HBr , finding $\Delta H = -22.56 \pm 0.5$ kcal/mole. Accepting $\Delta H_f^\circ (\text{HBr}, \text{g}) = -8.86$ kcal/mole (85), this leads to

$$\Delta H_f^\circ (\text{Bu}_2\text{BBr}, \text{liq}) = -83.8 \pm 2.6 \text{ kcal/mole} \quad (**)$$

Dibutylbromoborane (gas)

Skinner and Tees measured the vapor pressure over the range $20\text{--}90^\circ \text{C}$; $\Delta H_v = 12.1$ kcal/mole at 55°C , or 12.5 ± 0.3 kcal/mole at 25°C . Whence

$$\Delta H_f^\circ (\text{Bu}_2\text{BBr}, \text{g}) = -71.3 \pm 2.7 \text{ kcal/mole} \quad (**)$$

Dibutylboronic Acid (liquid)

Skinner and Tees measured the heats of hydrolysis of Bu_2BI and Bu_2BBr , finding -146.2 and -145.0 kcal/mole, respectively, for $\Delta H_f^\circ (\text{Bu}_2\text{BOH}, \text{liq})$. Taking the mean,

$$\Delta H_f^\circ (\text{Bu}_2\text{BOH}, \text{liq}) = -145.6 \pm 3 \text{ kcal/mole} \quad (**)$$

Dibutylboronic Acid (gas)

We have "estimated" $\Delta H_v = 15 \pm 2$ kcal/mole. Therefore,

$$\Delta H_f^\circ (\text{Bu}_2\text{BOH}, \text{g}) = -130.6 \pm 4 \text{ kcal/mole} \quad (**)$$

Dibutylchloroborane (liquid)

Skinner and Tees measured the heat of hydrolysis, $\Delta H = -18.54 \pm 0.1$ kcal/mole. Hence

$$\Delta H_f^\circ (\text{Bu}_2\text{BCl}, \text{liq}) = -98.7 \pm 3 \text{ kcal/mole} \quad (**)$$

Dibutylchloroborane (gas)

From vapor pressure measurements over the range 20–90°C, $\Delta H_v = 11.5$ kcal/mole at 55°C, or 12.0 ± 0.3 kcal/mole at 25°C. Consequently,

$$\Delta H_f^\circ (\text{Bu}_2\text{BCl}, \text{g}) = -86.7 \pm 3 \text{ kcal/mole} \quad (**)$$

Triisobutylborane (liquid)

Pope and Skinner (129) measured the heat of addition of diborane to isobutene. Accepting $\Delta H_f^\circ (\text{B}_2\text{H}_6, \text{g}) = 9.2 \pm 0.5$ kcal/mole, the derived value is

$$\Delta H_f^\circ (i\text{-Bu}_3\text{B}, \text{liq}) = -80.7 \pm 1.2 \text{ kcal/mole} \quad (**)$$

Triisobutylborane (gas)

Pope and Skinner estimated $\Delta H_v = 13.8 \pm 0.5$ kcal/mole, yielding

$$\Delta H_f^\circ (i\text{-Bu}_3\text{B}, \text{g}) = -66.9 \pm 1.3 \text{ kcal/mole} \quad (**)$$

Tri(sec-butyl)borane (liquid)

Haseley *et al.* (78) measured the heat of combustion, leading to

$$\Delta H_f^\circ [(sec\text{-Bu})_3\text{B}, \text{liq}] = -73 \pm 6 \text{ kcal/mole} \quad (**)$$

Tri(sec-butyl)borane (gas)

Pope and Skinner estimated $\Delta H_v = 14.3 \pm 0.5$ kcal/mole. Hence,

$$\Delta H_f^\circ [(sec\text{-Bu})_3\text{B}, \text{g}] = -58.7 \pm 6 \text{ kcal/mole} \quad (**)$$

Trihexylborane (liquid)

Bennett and Skinner (8) measured the heat of addition of diborane to hexene-1 in "diglyme" solution. From the results, the value

$$\Delta H_f^\circ (\text{Hx}_3\text{B}, \text{liq}) = -116.0 \pm 2.3 \text{ kcal/mole} \quad (**)$$

is derived.

Trihexylborane (gas)

Pope and Skinner estimated $\Delta H_v = 21.2 \pm 0.5$ kcal/mole; then

$$\Delta H_f^\circ (\text{Hx}_3\text{B}, \text{g}) = -94.8 \pm 2.5 \text{ kcal/mole} \quad (**)$$

Triheptylborane (liquid)

Bennett and Skinner measured the heat of addition of diborane to heptene-1 in "diglyme" solvent; hence

$$\Delta H_f^\circ (\text{Hp}_3\text{B}, \text{liq}) = -133.8 \pm 1.8 \text{ kcal/mole} \quad (**)$$

Triheptylborane (gas)

Pope and Skinner estimated $\Delta H_v = 24.4 \pm 0.5$ kcal/mole, leading to

$$\Delta H_f^\circ (\text{Hp}_3\text{B}, \text{g}) = -109.4 \pm 2 \text{ kcal/mole} \quad (**)$$

Trioctylborane (liquid)

Bennett and Skinner measured the heat of hydroboration of octene-1 in diglyme solvent, whereby

$$\Delta H_f^\circ (\text{Oc}_3\text{B}, \text{liq}) = -152.1 \pm 1.8 \text{ kcal/mole} \quad (**)$$

Trioctylborane (gas)

Pope and Skinner estimated $\Delta H_v = 27.6 \pm 0.5$ kcal/mole. Therefore,

$$\Delta H_f^\circ (\text{Oc}_3\text{B}, \text{g}) = -124.5 \pm 2 \text{ kcal/mole} \quad (**)$$

Alkylboron Difluorides (gas)

Steele *et al.* (163) obtained values for the dissociation energies, $D(\text{R}-\text{BF}_2)$, for $\text{R}=\text{Me}$, Et , $i\text{-Pr}$, and vinyl, from measurements of the appearance potentials of ions formed on electron impact. On combining these D values with the heats of formation of the radicals R , and an assumed value, $\Delta H_f^\circ (\text{BF}_2, \text{g}) = -135$ kcal/mole, the values

$$\Delta H_f^\circ (\text{MeBF}_2, \text{g}) = -199 \pm 3 \text{ kcal/mole}$$

$$\Delta H_f^\circ (\text{EtBF}_2, \text{g}) = -209 \pm 8 \text{ kcal/mole}$$

$$\Delta H_f^\circ (i\text{-PrBF}_2, \text{g}) = -212 \pm 8 \text{ kcal/mole}$$

$$\Delta H_f^\circ (\text{VnBF}_2, \text{g}) = -171 \pm 8 \text{ kcal/mole}$$

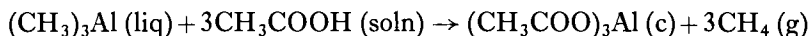
were derived.

Because of the lack of precision of the method and to assumptions which had to be made, the quoted error limits are substantial and do not permit a fruitful comparison of the individual values within the series.

Trimethylaluminum (liquid)

Long and Norrish (103) used a static bomb calorimeter to measure the heat of combustion. The solid product was shown to be corundum, little if any metal carbonate or hydroxide being formed. From the measured $\Delta H_c^\circ = -760.9 \pm 3$ kcal/mole, and ΔH_f° (Al_2O_3 , corundum) $= -400.5 \pm 3$ kcal/mole (111), the value ΔH_f° (Me_3Al , liq) $= -28.9 \pm 3$ kcal/mole is derived.

Mortimer and Sellers (123) used a rotating-bomb calorimeter to measure the heat of reaction of Me_3Al with acetic acid, in toluene solution



and obtained $\Delta H^\circ = -123.0 \pm 0.9$ kcal/mole. Separate studies were made to determine ΔH_f° (aluminum triacetate, c) $= -451.0 \pm 0.8$ kcal/mole. From these data ΔH_f° (Me_3Al , liq) $= -36.1 \pm 1.6$ kcal/mole.

Despite certain weaknesses in this calorimetric study (side-reaction corrections, small over-all temperature changes), the ΔH_f° value derived by Mortimer is preferred to the combustion value, for which the corrections to allow for incomplete combustion were somewhat arbitrary. The selected value is

$$\Delta H_f^\circ (\text{Me}_3\text{Al}, \text{liq}) = -36.0 \pm 2 \text{ kcal/mole} \quad (**)$$

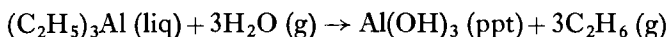
Trimethylaluminum (gas)

At 25°C , the vapor of trimethylaluminum is dimeric; McCullough *et al.* (118) measured ΔH_v at 25°C , finding 10.0 ± 0.05 kcal/mole. Hence, ΔH_f° (Me_6Al_2 , g) $= -62 \pm 4$ kcal/mole. The heat of dissociation of the dimer into monomer units is given as 20.2 kcal/mole dimer by Laubengayer and Gilliam (95), whereby

$$\Delta H_f^\circ (\text{Me}_3\text{Al}, \text{g}) = -21.0 \pm 2 \text{ kcal/mole} \quad (**)$$

Triethylaluminum (liquid)

Fowell and Mortimer (55) measured the heat of hydrolysis of triethylaluminum, and obtained $\Delta H^\circ = -154.8 \pm 2$ kcal/mole for the reaction



Accepting $\Delta H_f^\circ [\text{Al}(\text{OH})_3, \text{amorphous}] = -304 \pm 4 \text{ kcal/mole}$ (143), this gives

$$\Delta H_f^\circ (\text{Et}_3\text{Al}, \text{liq}) = -36.5 \pm 5 \text{ kcal/mole} \quad (**)$$

This determination is not very satisfactory, partly because of uncertainty in the heat of formation of $\text{Al}(\text{OH})_3$, and also because the gaseous products of hydrolysis were not analyzed but were assumed to be pure ethane.

Triethylaluminum (gas)

Laubengayer and Gilliam (95) measured the vapor pressure of liquid Et_3Al over the range $110\text{--}140^\circ\text{C}$; their data give $\Delta H_v = 16.6 \pm 0.4 \text{ kcal/mole}$, at 125°C . The vapor is *ca.* 12% associated to dimer. Fowell and Mortimer estimated $\Delta H_v = 17.5 \pm 0.5 \text{ kcal/mole}$ at 25°C for monomeric vapor; whence,

$$\Delta H_f^\circ (\text{Et}_3\text{Al}, \text{g}) = -19 \pm 5 \text{ kcal/mole} \quad (**)$$

Trimethylgallium (liquid)

Long and Sackman (108) measured the heat of combustion, using a static bomb calorimeter. The solid products of combustion contained Ga_2O_3 , metallic gallium, and soot. On correction for incomplete combustion, the value $\Delta H_c^\circ = -701.0 \pm 1.7 \text{ kcal/mole}$ was obtained. Assuming $\Delta H_f^\circ (\text{Ga}_2\text{O}_3, \text{c}, \beta) = -261.05 \pm 0.3 \text{ kcal/mole}$ (114), the derived value is $\Delta H_f^\circ (\text{Me}_3\text{Ga}, \text{liq}) = -19.1 \pm 2 \text{ kcal/mole}$.

Fowell and Mortimer (53) studied the reaction between Me_3Ga and iodine in benzene solution, and obtained $\Delta H = -60.5 \pm 2 \text{ kcal/mole}$ for the process



However, this reaction does not proceed to completion at room temperature, and it was necessary to extrapolate to obtain ΔH for complete iodination. Assuming (143) $\Delta H_f^\circ (\text{GaI}_3, \text{c}) = 51.2 \text{ kcal/mole}$ and (19) $\Delta H_f^\circ (\text{CH}_3\text{I}, \text{liq}) = -2.9 \pm 0.5 \text{ kcal/mole}$ the value $\Delta H_f^\circ (\text{Me}_3\text{Ga}, \text{liq}) = -12.1 \pm 3 \text{ kcal/mole}$ is derived.

The combustion value is perhaps the more convincing, and the selected value

$$\Delta H_f^\circ (\text{Me}_3\text{Ga}, \text{liq}) = -17 \pm 4 \text{ kcal/mole} \quad (**)$$

is weighted in its favor.

Trimethylgallium (gas)

From vapor pressure measurements over the range -36° to 56° C (88), $\Delta H_v = 7.8$ kcal/mole at 10° C, or 7.6 kcal/mole at 25° C, whence

$$\Delta H_f^{\circ} (\text{Me}_3\text{Ga, g}) = -9.2 \pm 4 \text{ kcal/mole} \quad (**)$$

Silicon Alkyls

Several investigators have measured heats of combustion of organosilicon compounds by static bomb methods, but the results obtained do not inspire confidence. Different investigators have failed to agree about the same compound, e.g., Tannenbaum, *et al.* (168) reported $\Delta H_c^{\circ} (\text{Me}_4\text{Si, liq}) = -920$ kcal/mole, whereas Lautsch (97) obtained -938.9 kcal/mole; for $\text{Et}_4\text{Si (liq)}$, Tannenbaum *et al.* found -1597 kcal/mole against -1584.0 kcal/mole by Lautsch. One reason for difficulty is that the silica formed on combustion tends to extinguish the flame and prevent complete combustion of the compound under investigation.

Good *et al.* (63) have recently described a rotating-bomb technique for investigating the combustion of silicon compounds which eliminates the serious complications arising from incomplete combustion. In the new approach, the silicon compound is admixed with a fluorine-containing substance (e.g., vinylidene fluoride polymer, benzotrifluoride) and burned in O_2 in the presence of water or dilute hydrofluoric acid. The combustion product after rotation of the bomb is a uniform solution of H_2SiF_6 in excess aqueous hydrofluoric acid: There are no solid products. If silica should form as a reaction intermediate, it is apparently rapidly dissolved by the HF resulting from combustion of the admixed organofluorine compound.

The new method has been applied to elemental silicon, yielding $\Delta H_f^{\circ} (\text{SiO}_2, \text{quartz}) = -217.5 \pm 0.5$ kcal/mole. This differs by some 8 kcal/mole from the value found by Humphrey and King (84) using the conventional bomb calorimetric method. The new value, however, is confirmed by Wise *et al.* (182), who obtained $\Delta H_f^{\circ} (\text{quartz}) = -217.75 \pm 0.34$ kcal/mole from measurements of the heat of combustion in fluorine of elemental silicon and of quartz.

Evidence of the unsuitability of the static bomb method for organosilicon compounds is further provided by the measurements of Good *et al.* (63) on the heat of combustion of hexamethyldisiloxane admixed with benzotrifluoride, from which the value $\Delta H_f^{\circ} (\text{Me}_3\text{SiOSiMe}_3, \text{liq}) = -194.7 \pm 1.3$

kcal/mole was derived. This corresponds to $\Delta H_c^\circ = -1415.5 \pm 1.5$ kcal/mole for the reaction



assuming $\Delta H_f^\circ (\text{SiO}_2, \text{amorp}) = -215.5$ kcal/mole. The heat of the above reaction, measured by Thompson (170) using a static bomb calorimeter, was -1401 kcal/mole. Dupree and Sinke (39) obtained essentially the same result, so that the static bomb investigations gave results of the order of 1% too low.

Many of the published heat of formation data on organosilicon compounds have been obtained by conventional bomb calorimetry, and cannot be accepted with confidence; they are omitted from this review.

Steele *et al.* (164) have obtained heats of formation for a number of alkylsilanes by measuring the appearance potentials of selected ions in the mass spectra of silane and alkyl silanes. For example, the appearance of SiH_2^+ from silane and RSiH_3 was adjudged to be caused by the processes



in which event,

$$\Delta H_f^\circ (\text{RSiH}_3) = \Delta H_f^\circ (\text{SiH}_4) + \Delta H_f^\circ (\text{RH}) - A_p(\text{RSiH}_3) + A_p(\text{SiH}_4)$$

where A_p is the appearance potential of SiH_2^+ .

Experiments using MeSiH_3 and EtSiH_3 led to

$$\Delta H_f^\circ (\text{MeSiH}_3, \text{g}) = -4 \pm 4 \text{ kcal/mole}$$

and

$$\Delta H_f^\circ (\text{EtSiH}_3, \text{g}) = -15 \pm 4 \text{ kcal/mole}$$

The error limits are necessarily large, because of lack of sharpness in the A_p measurements which, coupled with the limitations of the electron impact method, may account for the larger than expected difference between the quoted values for $\Delta H_f^\circ (\text{MeSiH}_3)$ and $\Delta H_f^\circ (\text{EtSiH}_3)$. The value for $\Delta H_f^\circ (\text{EtSiH}_3)$ is, however, confirmed by measurements of the appearance potential of Et^+ in the process



which yield $\Delta H_f^\circ = -16 \pm 4$ kcal/mole.

Tetraethylgermanium (liquid)

The heat of combustion of tetraethylgermanium using a static bomb calorimeter has been measured by Rabinovich *et al.* (136), and also by Pope and Skinner (130a). Rabinovich *et al.* reported $\Delta H_c^\circ = -1515.6 \pm 1.5$ kcal/mole, and stated that the solid product is GeO_2 (c, tetragonal). No mention was made of incomplete combustion. Pope and Skinner, however, found that although combustion is almost complete, small amounts of unburned Ge (and/or GeO) remain in the crucible. After correction for this, Pope and Skinner obtained $\Delta H_c^\circ = -1519.3 \pm 0.8$ kcal/mole. The difference from Rabinovich's value is not fully accounted for by the correction made for incomplete combustion of the metal.

Mah and Adami (116) have recently measured the heat of combustion of germanium metal, and found that the product is GeO_2 (c, hexagonal). The extent of incomplete combustion of metal in these experiments was *ca.* 1.7%. Combining Mah's $\Delta H_f^\circ (\text{GeO}_2, \text{c}) = -129.08 \pm 0.13$ kcal/mole with Pope's heat of combustion leads to

$$\Delta H_f^\circ (\text{Et}_4\text{Ge}, \text{liq}) = -45.3 \pm 1 \text{ kcal/mole} \quad (**)$$

Tetraethylgermanium (gas)

From vapor pressure data given by Rabinovich *et al.* (136), $\Delta H_v = 10.1 \pm 0.3$ kcal/mole at 70°C , or 10.7 kcal/mole at 25°C . Consequently,

$$\Delta H_f^\circ (\text{Et}_4\text{Ge}, \text{g}) = -34.6 \pm 1.1 \text{ kcal/mole} \quad (**)$$

Tetrapropylgermanium (liquid)

Pope and Skinner measured $\Delta H_c^\circ = -2144.5 \pm 0.4$ kcal/mole, leading to

$$\Delta H_f^\circ (\text{Pr}_4\text{Ge}, \text{liq}) = -69.6 \pm 0.6 \text{ kcal/mole} \quad (**)$$

Tetrapropylgermanium (gas)

Pope and Skinner estimated that $\Delta H_v = 14.7 \pm 1$ kcal/mole, hence

$$\Delta H_f^\circ (\text{Pr}_4\text{Ge}, \text{g}) = -54.9 \pm 1.2 \text{ kcal/mole} \quad (**)$$

Hexaethyldigermane (liquid)

Rabinovich *et al.* gave $\Delta H_c^\circ = -2321.0 \pm 2$ kcal/mole, corresponding to

$$\Delta H_f^\circ (\text{Et}_6\text{Ge}_2, \text{liq}) = -90.6 \pm 2.1 \text{ kcal/mole} \quad (**)$$

Hexaethyldigermane (gas)

Rabinovich *et al.* gave $\Delta H_v \sim 15$ kcal/mole, therefore,

$$\Delta H_f^\circ (\text{Et}_6\text{Ge}_2, \text{g}) = -75.6 \pm 3 \text{ kcal/mole} \quad (**)$$

Tetraalkyls of Tin

Davies *et al.* (37) studied the combustion of tin tetraalkyls by static bomb calorimetry, and found that virtually complete combustion can be attained. Analysis of the bomb gases after combustion showed that combustion of the carbon content was from 99.8–100% complete, and the solid combustion product was shown to be SnO_2 , only small amounts of unburned tin remaining admixed with it. Davies *et al.* obtained the results given in the table.

	ΔH_c° (kcal/mole)	ΔH_f° (kcal/mole)
Tetramethyltin (liq)	$-912.4 \pm 0.4_2$	$-12.5_3 \pm 0.45$
Trimethylethyltin (liq)	$-1071.2_2 \pm 0.55$	$-16.0_6 \pm 0.6$
Tetraethyltin (liq)	$-1551.4_8 \pm 0.56$	$-22.9_0 \pm 0.6$
Tetrapropyltin (liq)	-2173.3 ± 1.2	-50.6 ± 1.2
Tetrabutyltin (liq)	-2800.6 ± 1.7	-72.7 ± 1.8

The value $\Delta H_f^\circ (\text{SnO}_2, \text{c}) = -138.8_1 \pm 0.08$ kcal/mole (83) was accepted in deriving the ΔH_f° values above.

From vapor pressure data of Bullard and Haussman (17), Davies *et al.* calculated ΔH_v values at 25°C for Me_4Sn and Me_3SnEt , and used an extrapolation method to obtain ΔH_v for Et_4Sn , Pr_4Sn , and Bu_4Sn .

	ΔH_v (kcal/mole)	ΔH_f° (g) (kcal/mole)
Tetramethyltin	7.9 ± 0.3	-4.6 ± 0.6
Trimethylethyltin	$8.9_5 \pm 0.4$	-7.1 ± 0.7
Tetraethyltin	12.2 ± 0.5	-10.7 ± 0.8
Tetrapropyltin	16.0 ± 0.5	-34.6 ± 1.3
Tetrabutyltin	19.8 ± 0.5	-52.9 ± 1.9

Tetraphenyltin (crystalline)

Pope and Skinner (130*b*) measured $\Delta H_c^\circ = -3177.7 \pm 0.8$ kcal/mole; hence,

$$\Delta H_f^\circ (\text{Ph}_4\text{Sn}, \text{c}) = 98.5 \pm 0.9 \text{ kcal/mole} \quad (**)$$

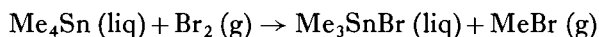
Tetraphenyltin (gas)

Carson *et al.* (20) measured the temperature variation of the vapor pressure of a tin tetraphenyl sample labeled with tritium by a modified Knudsen effusion technique; ΔH_v at $25^\circ \text{C} = 15.85$ kcal/mole. Consequently,

$$\Delta H_f^\circ (\text{Ph}_4\text{Sn}, \text{g}) = 114.3 \pm 1 \text{ kcal/mole} \quad (**)$$

Trimethyltin Bromide (liquid)

Pedley *et al.* (128) measured the heat of bromination of tetramethyltin



finding $\Delta H = -48.3 \pm 0.7$ kcal/mole. Accepting $\Delta H_f^\circ (\text{Me}_4\text{Sn}, \text{liq}) = -12.53 \pm 0.45$, $\Delta H_f^\circ (\text{Br}_2, \text{g}) = 7.39 \pm 0.03$ (166) and $\Delta H_f^\circ (\text{MeBr}, \text{g}) = -8.5 \pm 0.5$ kcal/mole, this leads to

$$\Delta H_f^\circ (\text{Me}_3\text{SnBr}, \text{liq}) = -44.9_4 \pm 1.0 \text{ kcal/mole} \quad (**)$$

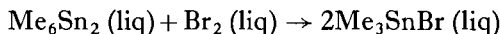
Trimethyltin Bromide (gas)

An estimate of ΔH_v from Trouton's rule and Wheland's equation (117) gives 11.3_5 kcal/mole (± 1.0) at 25°C , yielding

$$\Delta H_f^\circ (\text{Me}_3\text{SnBr}, \text{g}) = -33.6 \pm 1.5 \text{ kcal/mole} \quad (**)$$

Hexamethyldistannane (liquid)

Pedley *et al.* (128) measured the heat of bromination of hexamethyldistannane in cyclohexane solvent. For the idealized reaction



$\Delta H = -70.24 \pm 0.5$ kcal/mole, and accepting the value recommended above for the heat of formation of Me_3SnBr .

$$\Delta H_f^\circ (\text{Me}_6\text{Sn}_2, \text{liq}) = -19.6_4 \pm 2.1 \text{ kcal/mole} \quad (**)$$

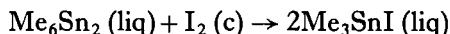
Hexamethyldistannane (gas)

ΔH_v , estimated from Trouton's rule (177), is 12.0 ± 1 kcal/mole at 25°C , hence

$$\Delta H_f^\circ (\text{Me}_6\text{Sn}_2, \text{g}) = -7.6_4 \pm 2.3 \text{ kcal/mole} \quad (**)$$

Trimethyltin Iodide (liquid)

Pedley *et al.* (128) measured the heat of iodination of hexamethyldistannane in cyclohexane solvent. For the idealized reaction



$\Delta H = -44.02 \pm 0.7$ kcal/mole. Therefore,

$$\Delta H_f^\circ (\text{Me}_3\text{SnI}, \text{liq}) = -31.8_3 \pm 1.1 \text{ kcal/mole} \quad (**)$$

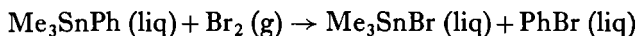
Trimethyltin Iodide (gas)

ΔH_v , estimated, is equal to 11.5 ± 1 kcal/mole. Therefore,

$$\Delta H_f^\circ (\text{Me}_3\text{SnI}, \text{g}) = -20.3_3 \pm 1.5 \text{ kcal/mole} \quad (**)$$

Trimethylphenyltin (liquid)

Pedley and Skinner (127) measured the heat of bromination, finding $\Delta H = -51.8 \pm 0.13$ kcal/mole for the reaction



Combining this with the recommended value for $\Delta H_f^\circ (\text{Me}_3\text{SnBr}, \text{liq})$, and with $\Delta H_f^\circ (\text{PhBr}, \text{liq}) = 13 \pm 2$ kcal/mole (151), we derive

$$\Delta H_f^\circ (\text{Me}_3\text{SnPh}, \text{liq}) = 12.5 \pm 2.3 \text{ kcal/mole} \quad (**)$$

Trimethylphenyltin (gas)

Davies *et al.* (37) estimated $\Delta H_v = 12.5 \pm 1$ kcal/mole; consequently,

$$\Delta H_f^\circ (\text{Me}_3\text{SnPh}, \text{g}) = 25.0 \pm 2.5 \text{ kcal/mole} \quad (**)$$

Trimethylbenzyltin (liquid)

From the heat of bromination (127), and assuming $\Delta H_f^\circ (\text{PhCH}_2\text{Br}, \text{liq}) = 3.8 \pm 0.5$ kcal/mole (3),

$$\Delta H_f^\circ (\text{Me}_3\text{SnCH}_2\text{Ph}, \text{liq}) = 5.6 \pm 1.2 \text{ kcal/mole} \quad (**)$$

Trimethylbenzyltin (gas)

Davies *et al.* estimated $\Delta H_v = 13.5 \pm 1$ kcal/mole. Hence, ΔH_f° (Me₃SnBz, g) = 19.1 ± 1.6 kcal/mole.

Trimethylvinyltin (liquid)

From measurements of the heat of bromination of trimethylvinyltin (127), and assuming ΔH_f° (CH₂=CHBr, g) = 18.7 ± 0.5 kcal/mole (93),

$$\Delta H_f^\circ (\text{Me}_3\text{SnCH}=\text{CH}_2, \text{liq}) = 12.1 \pm 1.2 \text{ kcal/mole} \quad (**)$$

Trimethylvinyltin (gas)

Davies *et al.* estimated $\Delta H_v = 8.9 \pm 0.5$ kcal/mole. Hence, ΔH_f° (Me₃SnVn, g) = 21.0 ± 1.3 kcal/mole.

Tributyltin Bromide (liquid)

From the heat of bromination of tetrabutyltin (127), and assuming ΔH_f° (BuBr, liq) = -34.5 ± 0.3 kcal/mole (14),

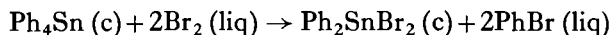
$$\Delta H_f^\circ (\text{Bu}_3\text{SnBr}, \text{liq}) = -85.5 \pm 2 \text{ kcal/mole} \quad (**)$$

Tributyltin Bromide (gas)

Davies *et al.* estimated $\Delta H_v = 20 \pm 3$ kcal/mole. Hence, ΔH_f° (Bu₃SnBr, g) = -65.5 ± 4 kcal/mole.

Diphenyltin Dibromide (crystalline)

Pedley and Skinner (127) measured the heat of bromination of tetraphenyltin, finding $\Delta H = -74.14 \pm 0.7$ kcal/mole for the reaction

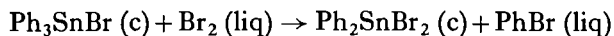


whence, assuming ΔH_f° (PhBr, liq) = 13 ± 2 kcal/mole,

$$\Delta H_f^\circ (\text{Ph}_2\text{SnBr}_2, \text{c}) = -1.6 \pm 3 \text{ kcal/mole} \quad (**)$$

Triphenyltin Bromide (crystalline)

The heat of bromination of triphenyltin bromide was measured by Pedley and Skinner (127),



$\Delta H = -35.15 \pm 0.35$ kcal/mole, and leads to

$$\Delta H_f^\circ (\text{Ph}_3\text{SnBr}, \text{c}) = -46.5 \pm 2.4 \text{ kcal/mole} \quad (**)$$

Hexaethyldistannane (liquid)

Rabinovich *et al.* (137) obtained $\Delta H_c^\circ = -2379 \pm 3$ kcal/mole, leading to

$$\Delta H_f^\circ (\text{Et}_6\text{Sn}_2, \text{liq}) = -52.0 \pm 3 \text{ kcal/mole} \quad (**)$$

Hexadiethylstannane (gas)

According to Rabinovich *et al.*, $\Delta H_v = 15 \pm 1$ kcal/mole; hence,

$$\Delta H_f^\circ (\text{Et}_6\text{Sn}_2, \text{g}) = -37.0 \pm 3.3 \text{ kcal/mole} \quad (**)$$

Dimethyltin Dichloride (crystalline)

From the measured heat of redistribution of SnMe_4 with SnCl_4 to form Me_2SnCl_2 (43), and $\Delta H_f^\circ (\text{SnCl}_4, \text{liq}) = -130.3$ kcal/mole (143),

$$\Delta H_f^\circ (\text{Me}_2\text{SnCl}_2, \text{c}) = -84.4 \pm 2 \text{ kcal/mole} \quad (**)$$

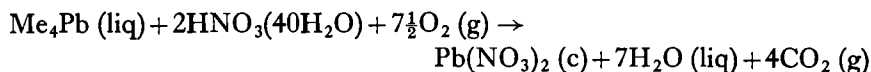
Dimethyltin Dichloride (gas)

The heat of sublimation may be estimated from the b.p. ($\Delta H_v \sim 12$ kcal/mole at 25°C), and an assumed 3 kcal/mole for the heat of fusion, hence, $\Delta H_s \sim 15 \pm 2$ kcal/mole, and

$$\Delta H_f^\circ (\text{Me}_2\text{SnCl}_2, \text{g}) = -69.4 \pm 3 \text{ kcal/mole} \quad (**)$$

Tetramethyllead (liquid)

The heat of combustion by the rotating-bomb method has been measured by Good *et al.* (66). The bomb contained nitric acid as solvent for the solid oxidation products of Pb, and the final solution was a uniform solution of $\text{Pb}(\text{NO}_3)_2$ in excess dilute nitric acid. For the idealized reaction



Good *et al.* obtained $\Delta H^\circ = -886.8 \pm 0.3$ kcal/mole. Assuming $\Delta H_f^\circ [\text{Pb}(\text{NO}_3)_2, \text{c}] = -107.35$ kcal/mole (143), this leads to

$$\Delta H_f^\circ (\text{Me}_4\text{Pb}, \text{liq}) = 23.5 \pm 0.3 \text{ kcal/mole} \quad (**)$$

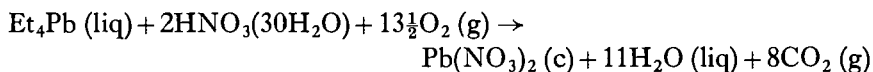
Tetramethyllead (gas)

Good *et al.* (66) obtained $\Delta H_v^\circ = 9.1$ kcal/mole at 25°C ; therefore,

$$\Delta H_f^\circ (\text{Me}_4\text{Pb}, \text{g}) = 32.6 \pm 0.3 \text{ kcal/mole} \quad (**)$$

Tetraethyllead (liquid)

Scott *et al.* (148) used the rotating-bomb method to obtain $\Delta H^\circ = -1525.6 \pm 0.6$ kcal/mole for the idealized reaction



Consequently,

$$\Delta H_f^\circ (\text{Et}_4\text{Pb, liq}) = 12.8 \pm 0.6 \text{ kcal/mole} \quad (**)$$

Tetraethyllead (gas)

Good *et al.* (66) state that $\Delta H_v = 13$ kcal/mole. Hence

$$\Delta H_f^\circ (\text{Et}_4\text{Pb, g}) = 25.8 \pm 0.6 \text{ kcal/mole} \quad (**)$$

Trimethylphosphine (liquid)

Long and Sackman (107) investigated the combustion of Me_3P by static bomb calorimetry, and found that the main product is phosphoric acid, only small quantities of phosphorous acid being formed. After correction for the latter, Long and Sackman obtained $\Delta H_c^\circ = -763.2 \pm 1.1$ kcal/mole for the pure reaction



Accepting Holmes' value (82), $\Delta H_f^\circ (\text{H}_3\text{PO}_4, \text{c}) = -305.7 \pm 1.0$ kcal/mole, this leads to

$$\Delta H_f^\circ (\text{Me}_3\text{P, liq}) = -29.6 \pm 1.5 \text{ kcal/mole} \quad (**)$$

Trimethylphosphine (gas)

Long and Sackman (109) measured the vapor pressure over the range -25° to 25°C : $\Delta H_v = 6.95$ at 0°C , 6.63 kcal/mole at 25°C . Thus,

$$\Delta H_f^\circ (\text{Me}_3\text{P, g}) = -23.0 \pm 1.5 \text{ kcal/mole} \quad (**)$$

Triethylphosphine (liquid)

Lautsch *et al.* (98) reported $\Delta H_c^\circ = -1237.6 \pm 3$ kcal/mole, corresponding to

$$\Delta H_f^\circ (\text{Et}_3\text{P, liq}) = -42.3 \pm 3 \text{ kcal/mole} \quad (**)$$

Few details were given, and the reliability of this determination is difficult to assess.

Triethylphosphine (gas)

From vapor pressure listed by Jordan (88), $\Delta H_v = 9.46$ kcal/mole at 25° C. Therefore,

$$\Delta H_f^\circ (\text{Et}_3\text{P}, \text{g}) = -32.8 \pm 3 \text{ kcal/mole} \quad (**)$$

Triphenylphosphine (crystalline)

The heat of combustion by static bomb calorimetry has been measured by Bedford and Mortimer (6), and also by Birr (12), who obtained $\Delta H_c^\circ = -2463.3 \pm 2.3$ kcal/mole and -2461.3 ± 3.6 kcal/mole, respectively. Bedford and Mortimer measured the amount of CO_2 produced on combustion, and corrected for incomplete combustion. Accepting their result as the more reliable, the derived heat of formation is

$$\Delta H_f^\circ (\text{Ph}_3\text{P}, \text{c}) = 53.8 \pm 2.5 \text{ kcal/mole} \quad (**)$$

Triphenylphosphine (gas)

From vapor pressure measurements over the range 200–300° C, Forward *et al.* (51) obtained $\Delta H_v = 17.0$ kcal/mole at 250° C; we have estimated that $\Delta H_v \sim 19.2$ kcal/mole at the melting point, and that *ca.* 3 kcal/mole should be added to allow for the heat of fusion; hence, $\Delta H_s = 22.2 (\pm 1)$ kcal/mole at 25° C, and

$$\Delta H_f^\circ (\text{Ph}_3\text{P}, \text{g}) = 76.0 \pm 2.7 \text{ kcal/mole} \quad (**)$$

Pentaphenylphosphole (crystalline)

Bedford *et al.* (5) reported $\Delta H_c^\circ = -4349.2 \pm 3.4$ kcal/mole, yielding

$$\Delta H_f^\circ \left[\begin{array}{c} \text{Ph} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{Ph} \quad \text{PPh} \end{array}, \text{c} \right] = 94.2 \pm 3.6 \text{ kcal/mole} \quad (**)$$

9-Phenyl-9-phosphafluorene (crystalline)

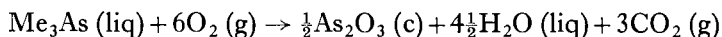
Bedford *et al.* obtained $\Delta H_c^\circ = -2385.6 \pm 2.0$ kcal/mole, leading to

$$\Delta H_f^\circ \left[\begin{array}{c} \text{Fluorene ring} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{PPh} \end{array}, \text{c} \right] = 45.4 \pm 2.3 \text{ kcal/mole} \quad (**)$$

Trimethylarsine (liquid)

Long and Sackman (106) investigated the combustion of Me_3As by static bomb calorimetry, and reported that the combustion products are a complex

mixture of solid As_2O_3 admixed with As_2O_4 , some unburned As and soot, and an aqueous solution of As(V) and As(III), varying in concentration from one part of the bomb to another. A method of analysis of the mixture was devised, and corrections made to the measured heat, leading to $\Delta H_c^\circ = -664.6 \pm 1.2$ kcal/mole for the "pure" combustion reaction



Combining this with $\Delta H_f^\circ (\text{As}_2\text{O}_3, \text{c}) = -157.0$ kcal/mole (143), Long and Sackman obtained

$$\Delta H_f^\circ (\text{Me}_3\text{As, liq}) = -3.5 \text{ kcal/mole} \quad (**)$$

This result could be misleading, since the accepted ΔH_f° values for both As_2O_3 and As_2O_5 are not well established, and might be in error by several kcal/mole (154)

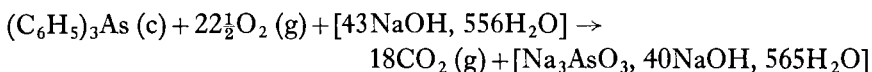
Trimethylarsine (gas)

From vapor pressure data of Long and Sackman (109), $\Delta H_v^\circ = 7.2$ kcal/mole. Hence,

$$\Delta H_f^\circ (\text{Me}_3\text{As, g}) = 3.7 \text{ kcal/mole} \quad (**)$$

Triphenylarsine (crystalline)

Mortimer and Sellers (123) measured the heat of combustion using rotating-bomb calorimetry: Ph_3As was burned in O_2 , in the presence of aqueous sodium hydroxide. The product was a homogeneous solution containing sodium arsenite, sodium arsenate, sodium carbonate, and sodium hydroxide. After analyzing the solution, corrections were made to allow for the heat effects due to formation of sodium carbonate and sodium arsenate. For the ideal reaction,



Mortimer and Sellers obtained $\Delta H^\circ = -2360.7 \pm 1.5$ kcal/mole, and deduced

$$\Delta H_f^\circ (\text{Ph}_3\text{As, c}) = 70.1 \pm 2 \text{ kcal/mole} \quad (**)$$

This value depends on the heat of formation of aqueous Na_3AsO_3 , which depends in turn on the accepted value for $\Delta H_f^\circ (\text{As}_2\text{O}_3, \text{c})$; the latter is not well established.

The heat of combustion of Ph_3As has also been measured by Birr (13),

using static bomb calorimetry. Birr's result,² $\Delta H_c^\circ = -2409.6 \pm 2.5$ kcal/mole (combustion to form As_2O_5) corresponds to $\Delta H_f^\circ = -96.2$ kcal/mole and is in poor agreement with the rotating-bomb result.

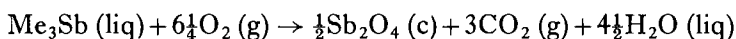
Triphenylarsine (gas)

From vapor pressure data (51), $\Delta H_v = 18.1$ kcal/mole at 250°C ; we estimate $\Delta H_v = 20.5$ kcal/mole at the m.p., and that ΔH_m is ~ 3 kcal/mole. Hence, $\Delta H_s = 23.5 \pm 1$ kcal/mole at 25°C , and

$$\Delta H_f^\circ (\text{Ph}_3\text{As}, \text{g}) = 93.6 \pm 2.3 \text{ kcal/mole} \quad (**)$$

Trimethylstibine (liquid)

Long and Sackman (105) reported that the combustion of trimethylantimony in a static bomb calorimeter gives Sb_2O_4 as the main solid product, admixed with Sb_2O_3 , unburned Sb metal, and some soot. After correction for the products of incomplete combustion, Long and Sackman obtained $\Delta H_c^\circ = -698.0 \pm 3.1$ kcal/mole for the "pure" combustion reaction



The heat of combustion of antimony metal has been measured by Mah (115), from which the value $\Delta H_f^\circ (\text{Sb}_2\text{O}_4, \text{c}) = -216.9 \pm 1.1$ kcal/mole was derived. Combining the latter with Long's heat of combustion,

$$\Delta H_f^\circ (\text{Me}_3\text{Sb}, \text{liq}) = -0.05 \pm 3.2 \text{ kcal/mole} \quad (**)$$

Trimethylstibine (gas)

From vapor pressure data given by Jordan (88), $\Delta H_v = 7.77$ kcal/mole at 0°C , or 7.45 kcal/mole at 25°C and

$$\Delta H_f^\circ (\text{Me}_3\text{Sb}, \text{g}) = 7.4 \pm 3.2 \text{ kcal/mole} \quad (**)$$

Triphenylstibine (crystalline)

Birr (12) measured the heat of combustion by static bomb calorimetry; his results give $\Delta H_c^\circ = -2392.5 \pm 2.5$ kcal/mole (formation of Sb_2O_4), leading to

$$\Delta H_f^\circ (\text{Ph}_3\text{Sb}, \text{c}) = 78.7 \pm 3 \text{ kcal/mole} \quad (**)$$

² Birr did not convert ΔE to ΔH in his paper, and made an arithmetical error in deriving ΔH_f° .

Triphenylstibine (gas)

From vapor pressure data (51), $\Delta H_v = 19.9$ kcal/mole at 250°C . We estimate $\Delta H_v = 22.4$ kcal/mole at the m.p., and allowing 3 kcal/mole for the heat of fusion, obtain $\Delta H_s = 25.4 \pm 1$ kcal/mole; hence,

$$\Delta H_f^\circ (\text{Ph}_3\text{Sb}, \text{g}) = 104.1 \pm 3.2 \text{ kcal/mole} \quad (**)$$

Trimethylbismuth (liquid)

The heat of combustion using a static bomb calorimeter was measured by Long and Sackman (104), who reported that combustion was incomplete, and that corrections were necessary to allow for unburned bismuth metal and soot. The corrected $\Delta H_c^\circ = -696.0 \pm 1.7$ kcal/mole, in conjunction with Mah's value $\Delta H_f^\circ (\text{Bi}_2\text{O}_3, \text{c}) = -137.16 \pm 0.3$ kcal/mole (113) leads to

$$\Delta H_f^\circ (\text{BiMe}_3, \text{liq}) = 37.8 \pm 2 \text{ kcal/mole} \quad (**)$$

Trimethylbismuth (gas)

From vapor pressure measurements by Bamford *et al.* (4), $\Delta H_v = 8.3$ kcal/mole. Hence,

$$\Delta H_f^\circ (\text{BiMe}_3, \text{g}) = 46.1 \pm 2 \text{ kcal/mole} \quad (**)$$

Triphenylbismuth (crystalline)

Birr (13) measured the heat of combustion, finding $\Delta H_c^\circ = -2386.2 \pm 2$ kcal/mole. Therefore,

$$\Delta H_f^\circ (\text{Ph}_3\text{Bi}, \text{c}) = 112.3 \pm 2 \text{ kcal/mole} \quad (**)$$

Triphenylbismuth (gas)

We have estimated $\Delta H_s \sim 26.5 \pm 2$ kcal/mole. Hence,

$$\Delta H_f^\circ (\text{Ph}_3\text{Bi}, \text{g}) = 1388 \pm 3 \text{ kcal/mole} \quad (**)$$

Diethylselenium (liquid)

Merten and Schlüter (119) measured the heat of combustion of Et_2Se /paraffin oil mixtures using a static bomb calorimeter. A combustion aid (oil, benzoic acid) was necessary to obtain complete oxidation of the $\text{Se} \rightarrow \text{SeO}_2$. In the "pure" reaction, $\Delta H_c^\circ = -749.7 \pm 0.7$ kcal/mole;

combination of this with $\Delta H_f^\circ (\text{SeO}_2, \text{c}) = -56.4_5 \pm 1 \text{ kcal/mole}$ (147)³ yields

$$\Delta H_f^\circ (\text{Et}_2\text{Se}, \text{liq}) = -24.6 \pm 1.3 \text{ kcal/mole} \quad (**)$$

Diethylselenium (gas)

An estimate from the boiling point (177) gives $\Delta H_v = 9.3 \text{ kcal/mole}$, yielding

$$\Delta H_f^\circ (\text{Et}_2\text{Se}, \text{g}) = -15.3 \pm 1.3 \text{ kcal/mole} \quad (**)$$

Dibenzylselenium (crystalline)

Merten and Schlüter (119) measured $\Delta H_c^\circ = -1849.5 \pm 5.7 \text{ kcal/mole}$, leading to,

$$\Delta H_f^\circ (\text{Bz}_2\text{Se}, \text{c}) = -1.9 \pm 6 \text{ kcal/mole} \quad (**)$$

Dibenzene-vanadium (crystalline)

Fischer and Reckziegel (48) measured the heat of combustion (static bomb), and reported $\Delta H_c^\circ = -1732.7 \pm 1.8 \text{ kcal/mole}$. No statement was made regarding the analysis of combustion products, or of corrections for incomplete combustion. Accepting $\Delta H_f^\circ (\text{V}_2\text{O}_5, \text{c}) = -373 \pm 2 \text{ kcal/mole}$ (152), the value

$$\Delta H_f^\circ [(\text{C}_6\text{H}_6)_2\text{V}, \text{c}] = 77 \pm 2.1 \text{ kcal/mole} \quad (**)$$

is derived.

Dibenzene-vanadium (gas)

Fischer and Reckziegel (48) state that vapor pressure measurements by Scherer indicated $\Delta H_s = 8.9 \text{ kcal/mole}$. This value seems altogether too low to be acceptable, and we prefer an estimated $\Delta H_s = 15 \pm 3 \text{ kcal/mole}$. Thus,

$$\Delta H_f^\circ [(\text{C}_6\text{H}_6)_2\text{V}, \text{g}] = 22.7 \pm 4 \text{ kcal/mole} \quad (**)$$

Chromium Hexacarbonyl (crystalline)

Cotton *et al.* (31) measured the heat of combustion (static bomb), and obtained $\Delta H_c^\circ = -443.1 \pm 0.5 \text{ kcal/mole}$; correction was made for incomplete combustion of Cr metal. Accepting $\Delta H_f^\circ (\text{Cr}_2\text{O}_3, \text{c}) = -272.7 \pm 0.4 \text{ kcal/mole}$ (110), this leads to

$$\Delta H_f^\circ [\text{Cr}(\text{CO})_6, \text{c}] = -257.6 \pm 0.6 \text{ kcal/mole} \quad (**)$$

³ From gray, hexagonal Se; -57.5 from amorphous Se.

Chromium Hexacarbonyl (gas)

From vapor pressure data of Hieber and Romberg (79), Cotton *et al.* derived $\Delta H_s = 17.2$ kcal/mole. Hence,

$$\Delta H_f^\circ [\text{Cr}(\text{CO})_6, \text{g}] = -240.4 \pm 1.0 \text{ kcal/mole} \quad (**)$$

Dibenzene-chromium (crystalline)

Fischer *et al.* (47) measured the heat of combustion, finding $\Delta H_c^\circ = -1696 \pm 8$ kcal/mole. The sample was coated with thymol to prevent oxidation prior to firing. Corrections for incomplete combustion of the Cr, and for the heat due to combustion of the thymol coating were made. The considerable scatter and uncertainty of the measured ΔH_c° suggests that the thymol coating was not fully effective.

Independent measurements by Fischer *et al.* (50) gave $\Delta H_c^\circ = -1725.4 \pm 2.0$ kcal/mole, differing from the Harvard value by nearly 30 kcal/mole. The smaller error limits imply that the Germans obtained a more reliable result, but as few details were given in the published report it is impossible to decide. We adopt an intermediate figure $\Delta H_c^\circ = -1710 \pm 15$ kcal/mole as the best available, corresponding to

$$\Delta H_f^\circ [(\text{C}_6\text{H}_6)_2\text{Cr}, \text{c}] = 35 \pm 15 \text{ kcal/mole} \quad (**)$$

Dibenzene-chromium (gas)

Fischer and Schreiner (49), from vapor pressure measurements over the range 86–98°C, derived $\Delta H_s = 18.7$ kcal/mole at 92°C, whereby

$$\Delta H_f^\circ [(\text{C}_6\text{H}_6)_2\text{Cr}, \text{g}] = 53.7 \pm 15 \text{ kcal/mole} \quad (**)$$

Dimesitylene-chromium (crystalline)

Fischer *et al.* (50) measured the heat of combustion, obtaining $\Delta H_c^\circ = -2638.0 \pm 3$ kcal/mole. The combustion samples were sealed (in argon) in gelatin capsules to prevent oxidation prior to firing. No statement was made of corrections made for incomplete combustion of the metal. The ΔH_c° value obtained corresponds to $\Delta H_f^\circ [(\text{C}_9\text{H}_{12})_2\text{Cr}, \text{c}] = -11.1 \pm 3$ kcal/mole.

Dimesitylene-chromium (gas)

Fischer *et al.* (50) reported $\Delta H_s = 15.4$ kcal/mole, obtained from vapor pressure studies over an unspecified temperature range. Accepting this, $\Delta H_f^\circ [(\text{C}_9\text{H}_{12})_2\text{Cr}, \text{g}] = 4.3 \pm 4$ kcal/mole.

Dipseudocumene-chromium (crystalline)

Fischer *et al.* (50) measured $\Delta H_c^\circ = -2640.0 \pm 1.9$ kcal/mole, leading to $\Delta H_f^\circ [(C_9H_{12})_2Cr, c] = -9.1 \pm 2$ kcal/mole.

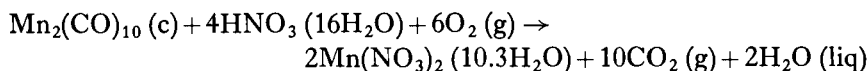
Dipseudocumene-chromium (gas)

Fischer *et al.* obtained $\Delta H_s = 8.0$ kcal/mole. This value, however, is barely credible and we prefer to assume that ΔH_s is the same as for dimesitylene chromium. Hence,

$$\Delta H_f^\circ [(C_9H_{12})_2Cr, g] = 6.3 \pm 3 \text{ kcal/mole} \quad (**)$$

Dimanganese Decacarbonyl (crystalline)

Good *et al.* (62) applied a rotating-bomb method to measure the heat of combustion; the solvent was aqueous nitric acid admixed with hydrogen peroxide. No solid products were formed, the final solution being manganous nitrate in excess nitric acid. For the idealized reaction



$\Delta H^\circ = -777.0 \pm 0.8$ kcal/mole. Accepting $\Delta H_f^\circ [Mn(NO_3)_2 \cdot (10.3H_2O)] = -148.75$ kcal/mole (143), this leads to

$$\Delta H_f^\circ [Mn_2(CO)_{10}, c] = -400.9 \pm 0.8 \text{ kcal/mole} \quad (**)$$

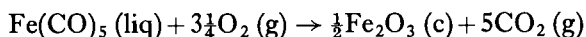
Dimanganese Decacarbonyl (gas)

Cotton and Monchamp (33) measured the vapor pressure over the range 102–146° C, and reported $\Delta H_s = 15 \pm 0.5$ kcal/mole. Slight decomposition of the compound occurred during the experiments. Accepting ΔH_s as reported,

$$\Delta H_f^\circ [Mn_2(CO)_{10}, g] = -385.9 \pm 1.3 \text{ kcal/mole} \quad (**)$$

Iron Pentacarbonyl (liquid)

Cotton *et al.* (32) measured the heat of combustion (static bomb). The solid product was mainly Fe_2O_3 (72–96%), and correction was made for incompletely oxidized Fe(II). The CO_2 was analyzed, and the slight deficit from theoretical assumed to be CO. For the “pure” combustion reaction



Cotton *et al.* obtained $\Delta H_c^\circ = 385.9 \pm 1.7$ kcal/mole; assuming ΔH_f° (Fe_2O_3 , c) = -196.5 kcal/mole, this leads to

$$\Delta H_f^\circ [\text{Fe}(\text{CO})_5, \text{liq}] = -182.6 \pm 1.7 \text{ kcal/mole} \quad (**)$$

Iron Pentacarbonyl (gas)

Trautz and Badstubner (171), from vapor pressure measurements, obtained $\Delta H_v = 9.6$ kcal/mole at 25°C . Hence,

$$\Delta H_f^\circ [\text{Fe}(\text{CO})_5, \text{g}] = -173.0 \pm 2 \text{ kcal/mole} \quad (**)$$

Iron Tetracarbonyl Dihalides (crystalline)

From heats of solution of $\text{Fe}(\text{CO})_4\text{Br}_2$ and FeBr_2 , and of $\text{Fe}(\text{CO})_4\text{I}_2$ and FeI_2 , by Hieber and Woerner (80), the values $\Delta H_f^\circ [\text{Fe}(\text{CO})_4\text{Br}_2, \text{c}] = -195.7$ kcal/mole and $\Delta H_f^\circ [\text{Fe}(\text{CO})_4\text{I}_2, \text{c}] = -178.5$ kcal/mole have been derived (143).

Ferrocene (crystalline)

Cotton and Wilkinson (34) measured the heat of combustion (static bomb). The solid products were a mixture of Fe_2O_3 and Fe_3O_4 . After correction for the mixed products, the value $\Delta H_f^\circ [(\text{C}_2\text{H}_5)_2\text{Fe}, \text{c}] = -33.8 \pm 1.3$ kcal/mole was derived.

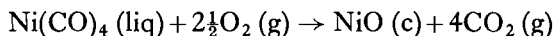
Ferrocene (gas)

Edwards and Kington (40) used a thermistor manometer to measure the vapor pressure over the range 20 – 30°C , and obtained $\Delta H_s = 17.53 \pm 0.1$ kcal/mole. Therefore,

$$\Delta H_f^\circ [\text{Fe}(\text{C}_5\text{H}_5)_2, \text{g}] = 51.3 \pm 1.3 \text{ kcal/mole} \quad (**)$$

Nickel Carbonyl (liquid)

Several attempts have been made to measure the heat of combustion of nickel carbonyl. The most satisfactory is that of Fischer *et al.* (46). They used benzoic acid as a combustion aid, tested the bomb gases after combustion for traces of unburned $\text{Ni}(\text{CO})_4$ and CO , and analyzed the solid product for unburned Ni metal (*ca.* 16–20%). For the pure combustion



Fischer *et al.* obtained $\Delta H_c^\circ = -282.2 \pm 0.5$ kcal/mole. Combination with $\Delta H_f^\circ (\text{NiO}, \text{c}) = -57.3 \pm 0.1$ kcal/mole (15) gives $\Delta H_f^\circ [\text{Ni}(\text{CO})_4, \text{liq}] = -151.3 \pm 0.5$ kcal/mole.

The heat of formation has also been obtained from studies on the equilibrium of formation from nickel and carbon monoxide gas. These investigations have been reviewed by Kipnis (89). The mean value from six independent measurements is ΔH_f° (liq) = -149.5 ± 2 kcal/mole. We adopt the average

$$\Delta H_f^\circ [\text{Ni}(\text{CO})_4, \text{liq}] = -150.4 \pm 1.5 \text{ kcal/mole} \quad (**)$$

as the best available.

Nickel Carbonyl (gas)

Kipnis (89) has recommended $\Delta H_v = 6.6 \pm 0.3$ kcal/mole, from consideration of available calorimetric and vapor pressure data, hence

$$\Delta H_f^\circ [\text{Ni}(\text{CO})_4, \text{g}] = -143.8 \pm 1.5 \text{ kcal/mole} \quad (**)$$

Dicyclopentadienylnickel (crystalline)

Wilkinson *et al.* (180) measured the heat of combustion (static bomb). Pellets of the compound, coated with paraffin wax, were found to burn satisfactorily, although less than half the nickel was oxidized to NiO. After correction for unburned nickel, and allowing for the heat of combustion of the wax coating, Wilkinson *et al.* derived

$$\Delta H_f^\circ [(\text{C}_5\text{H}_5)_2\text{Ni}, \text{c}] = 62.8 \pm 0.5 \text{ kcal/mole} \quad (**)$$

Dicyclopentadienylnickel (gas)

The heat of sublimation has not been measured, but is likely to be of the same order of magnitude as ΔH_s (ferrocene). Accepting $\Delta H_s = 18 \pm 1$ kcal/mole,

$$\Delta H_f^\circ [(\text{C}_5\text{H}_5)_2\text{Ni}, \text{g}] = 80.8 \pm 1.1 \text{ kcal/mole} \quad (**)$$

Molybdenum Hexacarbonyl (crystalline)

Cotton *et al.* (31) measured $\Delta H_c^\circ = -507.5 \pm 0.3$ kcal/mole. Corrections for incomplete oxidation of the Mo (to form MoO_3) were made. Assuming $\Delta H_f^\circ (\text{MoO}_3, \text{c}) = -178.16 \pm 0.11$ kcal/mole (111), this leads to

$$\Delta H_f^\circ [\text{Mo}(\text{CO})_6, \text{c}] = -235.0 \pm 0.4 \text{ kcal/mole} \quad (**)$$

Molybdenum Hexacarbonyl (gas)

Cotton *et al.* derived $\Delta H = 16.3$ kcal/mole from vapor pressure data of Hieber and Romberg (79). Thus $\Delta H_f^\circ [\text{Mo}(\text{CO})_6, \text{g}] = -218.7 \pm 1$ kcal/mole.

Dibenzene-molybdenum (crystalline)

Fischer and Reckziegel (48) measured $\Delta H_c^\circ = -1789.8 \pm 2.2$ kcal/mole. Few details were given, and no statement was made on the completeness of the combustion reaction. Accepting $\Delta H_f^\circ (\text{MoO}_3, \text{c}) = -178.16 \pm 0.11$ kcal/mole (111), this leads to

$$\Delta H_f^\circ [(\text{C}_6\text{H}_6)_2\text{Mo}, \text{c}] = 73.1 \pm 2.3 \text{ kcal/mole} \quad (**)$$

Dibenzene-molybdenum (gas)

Fischer and Reckziegel obtained $\Delta H_s = 22.6$ kcal/mole from vapor pressure studies, hence,

$$\Delta H_f^\circ [(\text{C}_6\text{H}_6)_2\text{Mo}, \text{g}] = 95.7 \pm 3 \text{ kcal/mole} \quad (**)$$

Tungsten Hexacarbonyl (crystalline)

Cotton *et al.* (31) measured $\Delta H_c^\circ = -537.8 \pm 0.3$ kcal/mole; correction for traces of incomplete combustion of tungsten metal were made. Assuming $\Delta H_f^\circ (\text{WO}_3, \text{c}) = -201.46 \pm 0.2$ kcal/mole (112), this gives

$$\Delta H_f^\circ [\text{W}(\text{CO})_6, \text{c}] = -228.0 \pm 0.4 \text{ kcal/mole} \quad (**)$$

Tungsten Hexacarbonyl (gas)

From vapor pressure of Hieber and Romberg (79) $\Delta H_s = 17.7$ kcal/mole. Therefore,

$$\Delta H_f^\circ [\text{W}(\text{CO})_6, \text{g}] = -210.3 \pm 1 \text{ kcal/mole} \quad (**)$$

TABLE III

HEATS OF FORMATION AND HEATS OF ATOMIZATION OF ORGANOMETALLIC COMPOUNDS

Compound	State	ΔH_f° (kcal/mole, 25° C)	ΔH_a° (kcal/mole, 25° C)
EtLi	c	-14.0 ± 1.3	—
	g	13.9 ± 1.4	(626.8)
BuLi	liq	-31.0 ± 2	—
	g	-5.4 ± 2.2	(1196.3)
MeMgI	ether, soln	-68.3 ± 0.6	—
Me ₂ Zn	liq	6.0 ± 2	—
	g	13.1 ± 2	672.5

TABLE III—*continued*

Compound	State	ΔH_f° (kcal/mole, 25° C)	ΔH_f° (kcal/mole, 25° C)
Et ₂ Zn	liq	4.0 ± 2	—
	g	13.0 ± 2	1222.8
Pr ₂ Zn	liq	-13.6 ± 6	—
Bu ₂ Zn	liq	-24.9 ± 6	—
Me ₂ Cd	liq	16.7 ± 0.2	—
	g	26.2 ± 0.3	655.0
Et ₂ Cd	liq	14.5 ± 0.4	—
	g	25.5 ± 0.7	1205.9
Me ₂ Hg	liq	14.0 ± 1	—
	g	22.3 ± 1	646.8
Et ₂ Hg	liq	6.5 ± 1	—
	g	17.2 ± 1	1202.1
Pr ₂ Hg	liq	-6.5 ± 2	—
	g	6.7 ± 2.1	1762.8
<i>i</i> -Pr ₂ Hg	liq	-3.4 ± 1	—
	g	9.4 ± 1.1	1760.1
Ph ₂ Hg	c	66.8 ± 1.5	—
	g	93.8 ± 1.6	2492.7
MeHgCl	c	-27.8 ± 0.6	—
	g	-12.3 ± 0.7	383.1
MeHgBr	c	-20.6 ± 0.6	—
	g	4.4 ± 0.7	373.0
MeHgI	c	-10.4 ± 0.6	—
	g	5.3 ± 0.7	362.1
EtHgCl	c	-34.0 ± 0.7	—
	g	-15.8 ± 1.0	661.7
EtHgBr	c	-26.0 ± 0.7	—
	g	-7.7 ± 1.0	651.3
EtHgI	c	-16.0 ± 0.8	—
	g	3.1 ± 1.1	639.4
PrHgCl	c	-40.6 ± 1.0	—
<i>i</i> -PrHgCl	c	-39.7 ± 0.6	—
PrHgBr	c	-32.7 ± 1.0	—
<i>i</i> -PrHgBr	c	-32.6 ± 0.6	—
PrHgI	c	-22.2 ± 1.0	—
<i>i</i> -PrHgI	c	-22.1 ± 0.6	—
PhHgCl	c	0.1 ± 1.2	—
	g	24.6 ± 1.5	1304.9
PhHgBr	c	7.8 ± 1.2	—
PhHgI	c	17.6 ± 1.2	—
Hg(CN) ₂	g	88.5 ± 2	494.0
Me ₃ B	liq	-34.1 ± 5.5	—

TABLE III—*continued*

Compound	State	ΔH_f° (kcal/mole, 25° C)	ΔH_a° (kcal/mole, 25° C)
Et ₃ B	g	-29.3 ± 5.5	1142.9
	liq	-45.3 ± 2.5	—
Bu ₃ B	g	-36.5 ± 2.5	1975.4
	liq	-82.5 ± 2.5	—
<i>i</i> -Bu ₃ B	g	-67.7 ± 2.6	3657.2
	liq	-80.7 ± 1.2	—
<i>sec</i> -Bu ₃ B	g	-66.9 ± 1.3	3656.4
	liq	-73 ± 6	—
Hx ₃ B	g	-58.7 ± 6	3648.2
	liq	-116.0 ± 2.3	—
Hp ₃ B	g	-94.8 ± 2.5	5334.9
	liq	-133.8 ± 1.8	—
Oc ₃ B	g	-109.4 ± 2	6174.8
	liq	-152.1 ± 1.8	—
Bu ₂ BCl	g	-124.5 ± 2	7015.2
	liq	-98.7 ± 3	—
Bu ₂ BBr	g	-86.7 ± 3	2552.6
	liq	-83.8 ± 2.6	—
Bu ₂ BI	g	-71.3 ± 2.7	2535.0
	liq	-66.3 ± 2.5	—
Bu ₂ BOH	g	-53.3 ± 2.6	2515.8
	liq	-145.6 ± 3	—
MeBF ₂	g	-130.6 ± 4	2679.3
	g	-199 ± 3	695.9
EtBF ₂	g	-209 ± 8	981.0
	g	-212 ± 8	1259.1
<i>i</i> -PrBF ₂	g	-171 ± 8	838.8
	g	-171 ± 8	838.8
Me ₃ Al	g	-36.0 ± 2	—
	liq	-21.0 ± 2	1080.6
Me ₃ Al ₂	g	-62 ± 4	2180.2
	g	-62 ± 4	2180.2
Et ₃ Al	g	-36.5 ± 5	—
	liq	-19 ± 5	1903.9
Me ₃ Ga	g	-17 ± 4	—
	liq	-9.2 ± 4	1059.8
(Me ₃ Si) ₂ O	g	-9.2 ± 4	1059.8
	liq	-194.7 ± 1.3	—
EtSiH ₃	g	-185.8 ± 1.3	2317.0
	g	-15.5 ± 4	882.5
Et ₄ Ge	g	-45.3 ± 1	—
	liq	-34.6 ± 1.1	2534.0
Pr ₄ Ge	g	-69.6 ± 0.6	—
	liq	-54.9 ± 1.2	3654.7
Et ₆ Ge ₂	g	-90.6 ± 2.1	—
	liq	-75.6 ± 3	3869.8

TABLE III—*continued*

Compound	State	ΔH_f° (kcal/mole, 25° C)	ΔH_a° (kcal/mole, 25° C)
Me ₄ Sn	liq	-12.5 ± 0.5	—
	g	-4.6 ± 0.6	1385.4
Et ₄ Sn	liq	-22.9 ± 0.6	—
	g	-10.7 ± 0.8	2491.9
Pr ₄ Sn	liq	-50.6 ± 1.2	—
	g	-34.6 ± 1.3	3616.2
Bu ₄ Sn	liq	-72.7 ± 1.8	—
	g	-52.9 ± 1.9	4734.9
Me ₃ EtSn	liq	-16.1 ± 0.6	—
	g	-7.1 ± 0.7	1663.0
Me ₃ VnSn	liq	12.1 ± 1.2	—
	g	21.0 ± 1.3	1530.7
Me ₃ PhSn	liq	12.5 ± 2.3	—
	g	25.0 ± 2.5	2314.5
Me ₃ BzSn	liq	5.6 ± 1.2	—
	g	19.1 ± 1.6	2595.5
Ph ₄ Sn	c	98.5 ± 0.9	—
	g	114.3 ± 1	5101.3
Me ₆ Sn ₂	liq	-19.6 ± 2.1	—
	g	-7.6 ± 2.3	2114.8
Et ₆ Sn ₂	liq	-52.0 ± 3	—
	g	-37.0 ± 3.3	—
Me ₃ SnBr	liq	-44.9 ± 1.0	—
	g	-33.6 ± 1.5	1113.9
Me ₃ SnI	liq	-31.8 ± 1.1	—
	g	-20.3 ± 1.5	1099.4
Bu ₃ SnBr	liq	-85.5 ± 2	—
	g	-65.5 ± 4	3621.7
Ph ₃ SnBr	c	-46.5 ± 2.4	—
Ph ₂ SnBr ₂	c	-1.6 ± 3	—
Me ₂ SnCl ₂	c	-84.4 ± 2	—
	g	-69.4 ± 3	853.6
Me ₄ Pb	liq	23.5 ± 0.3	—
	g	32.6 ± 0.3	1323.0
Et ₄ Pb	liq	12.8 ± 0.6	—
	g	25.8 ± 0.6	2430.1
Me ₃ P	liq	-29.6 ± 1.5	—
	g	-23.0 ± 1.5	1080.4
Et ₃ P	liq	-42.3 ± 3	—
	g	-32.8 ± 3	1915.5
Ph ₃ P	c	53.8 ± 2.5	—
	g	76.0 ± 2.7	3857.2
Pentaphenylphosphole	c	94.2 ± 3.6	—

TABLE III—continued

Compound	State	ΔH_f° (kcal/mole, 25° C)	ΔH_a° (kcal/mole, 25° C)
9-Phenyl-9-phosphafluorene	c	45.4 ± 2.3	—
Me ₃ As	liq	-3.5 ± 1.2	—
	g	3.7 ± 1.2	1046.9
Ph ₃ As	c	70.1 ± 2	—
	g	93.6 ± 2.3	3833.1
Me ₃ Sb	liq	-0.1 ± 3.2	—
	g	7.4 ± 3.2	1037.3
Ph ₃ Sb	c	78.7 ± 3	—
	g	104.1 ± 3.2	3816.6
Me ₃ Bi	liq	37.8 ± 2	—
	g	46.1 ± 2	985.0
Ph ₃ Bi	c	112.3 ± 2	—
	g	138.8 ± 3	3768.4
Et ₂ Se	liq	-24.6 ± 1.3	—
	g	-15.3 ± 1.3	1269.3
Bz ₂ Se	c	-1.9 ± 6	—
(C ₆ H ₅) ₂ V	c	7.7 ± 2.1	—
	g	22.7 ± 4	2776.3
Cr(CO) ₆	c	-257.6 ± 0.6	—
	g	-240.4 ± 1	1718.2
(C ₆ H ₅) ₂ Cr	c	35 ± 15	—
	g	53.7 ± 15	2717.3
Dimesitylene Cr	c	-11.1 ± 3	—
	g	4.3 ± 4	4417.3
Dipseudocumene Cr	c	-9.1 ± 2	—
	g	6.3 ± 3	4415.3
Mn ₂ (CO) ₁₀	c	-400.9 ± 0.8	—
	g	-385.9 ± 1.3	2823.9
Fe(CO) ₅	liq	-182.6 ± 1.7	—
	g	-173.0 ± 2	1424.8
(C ₅ H ₅) ₂ Fe	c	33.8 ± 1.3	—
	g	51.3 ± 1.3	2278.2
Fe(CO) ₄ Br ₂	c	-195.7	—
Fe(CO) ₄ I ₂	c	-178.5	—
Ni(CO) ₄	liq	-150.4 ± 1.5	—
	g	-143.8 ± 1.5	1168.4
(C ₅ H ₅) ₂ Ni	c	62.8 ± 0.5	—
	g	80.8 ± 1.1	2252.0
Mo(CO) ₆	c	-235.0 ± 0.4	—
	g	-218.7 ± 1	1759.0
(C ₆ H ₅) ₂ Mo	c	73.1 ± 2.3	—
	g	95.7 ± 3	2737.8
W(CO) ₆	c	-228.0 ± 0.4	—
	g	-210.3 ± 1	1794.9

V

METAL-CARBON BOND ENERGY TERM VALUES

The Allen equation [Eq. (4)], modified by the addition of one or more terms to allow for steric repulsions (where necessary), has been shown by Skinner (153) to reproduce very satisfactorily the available heats of formation and ΔH_a° values of paraffin hydrocarbons from CH_4 through the octanes and nonanes. The parameters in Eq. (4) were evaluated empirically as

$$\begin{aligned} B_{\text{CC}} &= 78.84 \text{ kcal/mole} & B_{\text{CH}} &= 99.29 \text{ kcal/mole} \\ \Gamma_{\text{CCC}} &= 2.58 \text{ kcal/mole} & \Delta_{\text{CCC}} &= -0.55 \text{ kcal/mole} \end{aligned}$$

McCullough and Good (117) have similarly shown that the Allen scheme correlates very well with the available heat of formation data on alkyl thiols, dialkyl sulfides, and dialkyl disulfides. The recommended "effective" term values are

$$\begin{aligned} B_{\text{CS}} &= 65.19 \text{ kcal/mole} \\ B_{\text{SS}} &= 57.0 \text{ kcal/mole} \\ B_{\text{SH}} &= 87.35 \text{ kcal/mole} \end{aligned}$$

and the interaction parameters are

$$\begin{aligned} \Gamma_{\text{CCS}} &= 3.30 \text{ kcal/mole} \\ \Gamma_{\text{CSC}} &= 2.97 \text{ kcal/mole} \\ \Gamma_{\text{CSS}} &= 4.45 \text{ kcal/mole} \\ \Delta_{\text{CCS}} &= -1.2 \text{ kcal/mole} \end{aligned}$$

Applied to a metallic alkyl, $\text{M}(\text{C}_n\text{H}_{2n+1})_m$, the Allen scheme leads to the formula

$$\begin{aligned} \Delta H_a^\circ (\text{calc.}) &= mB_{\text{MC}} + m(n-1)B_{\text{CC}} + m(2n+1)B_{\text{CH}} + b_3\Gamma_{\text{CCC}} + \\ &\quad + b_3'\Gamma_{\text{CCM}} + b_3''\Gamma_{\text{CMC}} + c_4\Delta_{\text{CCC}} + c_4'\Delta_{\text{CCM}} + \\ &\quad + c_4''\Delta_{\text{CCM}}^{\text{M}} - [S] \end{aligned} \quad (6)$$

where B_{MC} is the effective M—C bond energy, Γ_{CCM} and Γ_{CMC} the bond interactions C—C—M and C—M—C (b_3' and b_3'' the number of such terms), Δ_{CCM} the trio interaction arising from

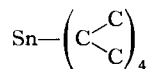


and $\Delta_{\text{CCC}}^{\text{M}}$ from



(c_4' and c_4'' the number of these terms), and $[S]$ the corrections, when

necessary, for steric repulsion in the molecule. To illustrate, consider tetrapropyltin, represented by $\text{Sn}-(\text{CCC})_4$, and tetraisopropyltin,



The Allen equations, respectively, are

$$\Delta H_a^\circ = 4B_{\text{SnC}} + 8B_{\text{CC}} + 28B_{\text{CH}} + 4\Gamma_{\text{CCC}} + 4\Gamma_{\text{CCSn}} + 6\Gamma_{\text{CSnC}} + 4\Delta_{\text{CCC}}^{\text{Sn}} - [S(i)] \quad (i)$$

$$\Delta H_a^\circ = 4B_{\text{SnC}} + 8B_{\text{CC}} + 28B_{\text{CH}} + 4\Gamma_{\text{CCC}} + 8\Gamma_{\text{CCSn}} + 6\Gamma_{\text{CSnC}} + 4\Delta_{\text{CCC}}^{\text{Sn}} + 4\Delta_{\text{CCSn}} - [S(ii)] \quad (ii)$$

Values of the bond energy parameters in Eq. (6) have to be obtained empirically by fitting the available ΔH_a° data to the equations, and the results of this exercise are given in Table IV. The many gaps in Table IV, and the questionable accuracy of several of the quoted values reflect the

TABLE IV
BOND ENERGY TERM VALUES AND ALLEN PARAMETERS OF METAL-CARBON BONDS^a

Term Values	Parameters
$B_{\text{LiC}} + \Gamma_{\text{CCLi}} = (56.3 \pm 5)$	—
$B_{\text{ZnC}} + \frac{1}{2}\Gamma_{\text{CZnC}} = 38.4$	$\Gamma_{\text{CCZn}} = -2.3$
$B_{\text{CdC}} + \frac{1}{2}\Gamma_{\text{CCdC}} = 29.6$	$\Gamma_{\text{CCCd}} = -2.0$
$B_{\text{HgC}} + \frac{1}{2}\Gamma_{\text{CHgC}} = 25.5$	$\Gamma_{\text{CCHg}} = 0.2$
	$\Delta_{\text{CCHg}} = -1.5$
$B_{\text{BC}} + \Gamma_{\text{CBC}} + \frac{1}{3}\Delta_{\text{CCC}}^{\text{B}} = 82.5$	$\Gamma_{\text{CCB}} = 0.7$
	$\Delta_{\text{CCB}} = -1.1$
$B_{\text{AlC}} + \Gamma_{\text{CAIC}} + \frac{1}{3}\Delta_{\text{CCC}}^{\text{Al}} = 62.3$	$\Gamma_{\text{CCAAl}} = -3.0$
$B_{\text{GaC}} + \Gamma_{\text{CGaC}} + \frac{1}{3}\Delta_{\text{CCC}}^{\text{Ga}} = 55.4$	—
$B_{\text{GeC}} + \frac{3}{2}\Gamma_{\text{CGeC}} + \Delta_{\text{CCC}}^{\text{Ge}} + \Gamma_{\text{CCGe}} = 58.3$	—
$B_{\text{SnC}} + \frac{3}{2}\Gamma_{\text{CSnC}} + \Delta_{\text{CCC}}^{\text{Sn}} = 48.5$	$\Gamma_{\text{CCSn}} = -0.3$
$B_{\text{PbC}} + \frac{3}{2}\Gamma_{\text{CPbC}} + \Delta_{\text{CCC}}^{\text{Pb}} = 32.9$	$\Gamma_{\text{CCPb}} = -0.8$
$B_{\text{PC}} + \Gamma_{\text{CCP}} + \frac{1}{3}\Delta_{\text{CCC}}^{\text{P}} = 62.3$	$\Gamma_{\text{CCP}} = 0.9$
$B_{\text{AsC}} + \Gamma_{\text{CAAsC}} + \frac{1}{3}\Delta_{\text{CCC}}^{\text{As}} = 51.1$	—
$B_{\text{SbC}} + \Gamma_{\text{CSbC}} + \frac{1}{3}\Delta_{\text{CCC}}^{\text{Sb}} = 47.9$	—
$B_{\text{BiC}} + \Gamma_{\text{CBiC}} + \frac{1}{3}\Delta_{\text{CCC}}^{\text{Bi}} = 30.5$	—
$B_{\text{SeC}} + \frac{1}{2}\Gamma_{\text{CSeC}} + \Gamma_{\text{CCSe}} = 59.4$	—

^a Energies given in kcal/mole.

lack and the inadequacy of experimental data. It is noteworthy that the values Γ_{CCX} become small, and even negative, the more electropositive the atom X.

VI

MEAN BOND DISSOCIATION ENERGIES OF METAL-CARBON BONDS

The *mean* bond dissociation energies in compounds MR_n , defined by $\bar{D}(\text{M}-\text{R}) = \Delta H^\circ/n$ [Eq. (5)], are readily obtained provided the heats of formation ΔH_f° (MR_n , g), ΔH_f° (M, g) and ΔH_f° (R, g) are known. The values listed in Table V are derived from the heat of formation data listed

TABLE V
 $\bar{D}(\text{M}-\text{R})$ VALUES IN MR_n

Compound	\bar{D} (kcal/mole)	Compound	\bar{D} (kcal/mole)
Li—Et	50.0 ± 2.4	Pb—Me	36.5 ± 1
Li—Bu	59.3 ± 3	Pb—Et	30.8 ± 2
Zn—Me	42.0 ± 1.5	P—Me	65.8 ± 1.2
Zn—Et	34.6 ± 2.2	P—Et	61.6 ± 2.3
Cd—Me	33.3 ± 1	P—Ph	71.9 ± 2.3
Cd—Et	26.1 ± 2	As—Me	54.8 ± 1.5
Hg—Me	29.2 ± 1.1	As—Ph	63.8 ± 2.3
Hg—Et	24.2 ± 2.1	Sb—Me	51.5 ± 1.6
Hg—Pr	24.5 ± 2.2	Sb—Ph	58.3 ± 2.3
Hg— <i>i</i> -Pr	21.0 ± 2.2	Bi—Me	34.1 ± 1.3
Hg—Ph	32.4 ± 2.1	Bi—Ph	42.2 ± 2.3
B—Me	86.8 ± 2.7	Se—Et	57.8 ± 1.6
B—Et	81.7 ± 2.7	V-benzene	70.0 ± 2
B—Bu	82.1 ± 2.7	Cr—carbonyl	29.5 ± 0.3
Al—Me	66.0 ± 1.2	Cr—benzene	40.5 ± 8
Al—Et	57.8 ± 2.6	Cr—mesitylene	41.5 ± 2
Ga—Me	59.1 ± 2	Cr— <i>p</i> -cumene	41.0 ± 2
Ge—Et	56.7 ± 2	Fe—carbonyl	28.0 ± 0.5
Ge—Pr	56.8 ± 2	Fe—cyclo- C_5	69.5 ± 10
Sn—Me	52.1 ± 1.1	Ni—carbonyl	35.2 ± 0.5
Sn—Et	46.2 ± 2.1	Ni—cyclo- C_5	56.6 ± 10
Sn—Pr	47.2 ± 2.1	Mo—carbonyl	36.3 ± 0.5
Sn—Bu	46.7 ± 2.1	Mo—benzene	50.7 ± 2
Sn—Ph	61.4 ± 2.1	W—carbonyl	42.3 ± 0.5

in Tables I, II, and III, and from the established values (142) ΔH_f° (CO, g) = -26.42 kcal/mole, ΔH_f° (C₆H₆, g) = 19.82 kcal/mole, ΔH_f° (1,2,4-trimethylbenzene, g) = -3.33 kcal/mole, ΔH_f° (1,3,5-trimethylbenzene, g) = -3.84 kcal/mole.

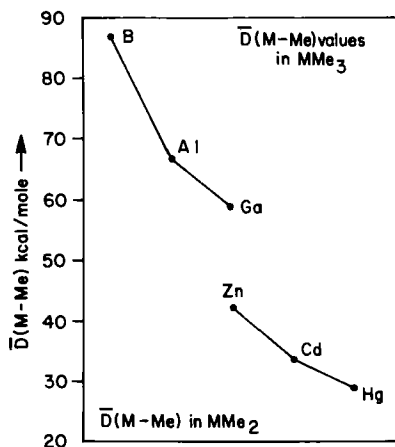


FIG. 1. $\bar{D}(M-Me)$ values for B, Al, Ga, Zn, Cd, and Hg.

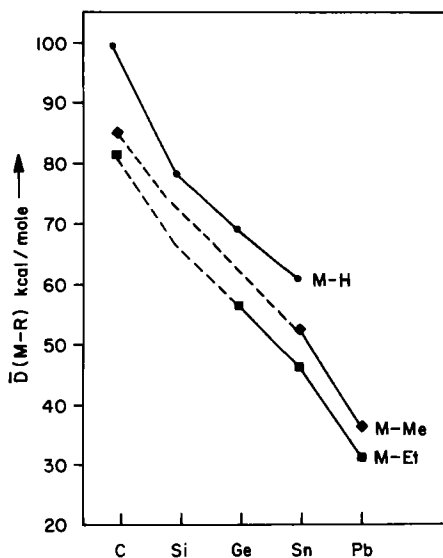


FIG. 2. $\bar{D}(M-R)$ values for C, Si, Ge, Sn, and Pb.

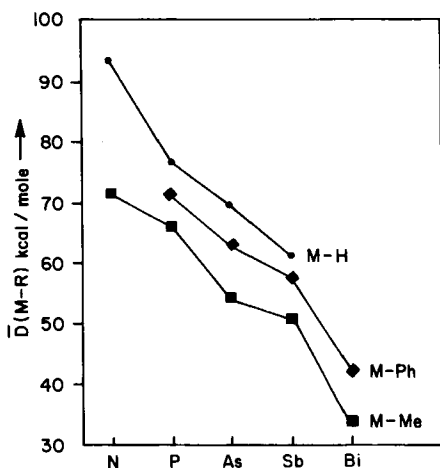


FIG. 3. $\bar{D}(\text{M}-\text{R})$ values for N, P, As, Sb, and Bi.

Certain trends are apparent, despite the limited data available; these are:

- (i) $\bar{D}(\text{M}-\text{Me}) > \bar{D}(\text{M}-\text{Et})$, usually by as much as 5 kcal/mole.
- (ii) $\bar{D}(\text{M}-\text{Ph}) > \bar{D}(\text{M}-\text{Me})$, by several kcal/mole.
- (iii) $\bar{D}(\text{M}-\text{R})$ values fall progressively as M descends a given group (e.g., Group IV, $\bar{D}(\text{C}-\text{R}) > \bar{D}(\text{Si}-\text{R}) > \bar{D}(\text{Ge}-\text{R}) > \bar{D}(\text{Sn}-\text{R}) > \bar{D}(\text{Pb}-\text{R})$).
- (iv) The $\bar{D}(\text{M}-\text{R})$ values descending a given group roughly parallel the corresponding values $\bar{D}(\text{M}-\text{H})$.

Figures 1-3 illustrate these points graphically.

- (v) Contrary to (iii), $\bar{D}(\text{M}-\text{CO})$ increases in descending the group $\text{Cr} \rightarrow \text{Mo} \rightarrow \text{W}$.

VII

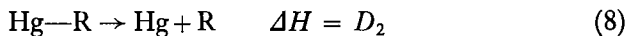
METAL-CARBON BOND DISSOCIATION ENERGIES

The most extensive studies on the dissociation energies of metal-carbon bonds have been made on organomercury compounds, in particular on the dialkyls of mercury. The mean bond dissociation energies, $\bar{D}(\text{Hg}-\text{R})$, are of the order 20-30 kcal/mole, implying that $\text{Hg}-\text{C}$ is normally rather a weak bond, and that mercury alkyls should decompose easily on heating. Although this is the case, it has transpired that $\text{Hg}-\text{C}$ bonds are more

stable to heat than indicated by the \bar{D} values, and that the energy required to initiate disruption, i.e.,



is decidedly more than required to complete the break-up of the molecule, i.e.,

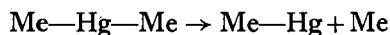


The inequality of D_1 and D_2 values in mercuric compounds was first demonstrated by Wieland (178) from studies on mercuric chloride. From an investigation of the photochemical decomposition of gaseous HgCl_2 , Wieland obtained $D_1(\text{Cl—HgCl}) = 81 \pm 1$ kcal/mole, whereas analysis of the spectrum of gaseous HgCl showed that $D_2(\text{Hg—Cl})$ is only 24 kcal/mole. The sum ($D_1 + D_2$) is obtainable independently from the thermochemical determination, $\Delta H_f^\circ (\text{HgCl}_2, \text{g}) = -33.4$ kcal/mole; therefore, $\Delta H_a^\circ = (D_1 + D_2) = 106$ kcal/mole, in close agreement with the sum of Wieland's D_1 and D_2 values. Measurements of $D_2(\text{Hg—Br})$ and $D_2(\text{Hg—I})$ by Wieland and Herczog (179) from analyses of the HgBr and HgI spectra, in conjunction with thermochemical ΔH_a° values for gaseous HgBr_2 and HgI_2 , show similar inequalities in D_1 and D_2 in these molecules. These values are given in the following tabulation

Molecule	$(D_1 + D_2)$ thermochemical	D_1 obs.	D_2 obs.	$(D_1 + D_2) - D_2$
HgCl_2	106 ± 2	81 ± 1	24	82 ± 2
HgBr_2	89 ± 2	—	17	72 ± 2
HgI_2	69 ± 2	—	8 ± 1	61 ± 2

The kinetics of thermal decomposition of dimethylmercury and diethylmercury were first studied by Gowenlock *et al.* (68), using a flow method with low pressure of alkyl in N_2 as carrier gas, and short contact times. The velocity constants were slightly pressure dependent, but the frequency factors had the normal value for unimolecular decomposition, $\log_{10} \nu \sim 13$. Price and Trotman-Dickenson (131) used the toluene carrier gas technique in a reinvestigation of the pyrolysis kinetics of dimethylmercury, and confirmed the earlier findings. Laurie and Long (96) studied the thermal decomposition of HgMe_2 vapor in a static system, at pressures of 70–80 mm

(in the flow systems, the partial pressure of alkyl was below 1 mm), and found that over the temperature range 294–333° C the decomposition was homogeneous and first order, and the activation energy was the same as reported by Gowenlock *et al.* with frequency factor, $\log_{10} \nu \sim 14$. Above 333° C, the kinetic behavior changes in the static system. The substantial agreement between these different studies made it seem clear that the thermal decomposition involved the process



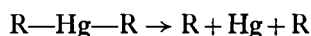
as the initial rate-determining step, so that the experimental activation energy ($E_{\text{act}} = 51.5 \pm 2$ kcal/mole) should be a direct measure of D_1 in HgMe_2 . In this event, D_2 is determined as 6.9 ± 3 kcal/mole, since the thermochemistry of HgMe_2 requires that $(D_1 + D_2)$ should be 58.4 ± 2.2 kcal/mole. The small value for $D_2(\text{Hg—Me})$ is not unexpected, by analogy with the well-established value $D_2(\text{Hg—H}) = 8.6$ kcal/mole (61).

Studies of the kinetics of pyrolysis of higher mercury alkyls (Pr_2Hg , Bu_2Hg , *i*- Pr_2Hg , Ph_2Hg), however, have shown that the pattern is different from that found with Me_2Hg (and Et_2Hg), in that the frequency factors are abnormally high, $\log_{10} \nu = 16 \pm 0.7$. Warhurst (176) has referred to the latter as “class II” decompositions in contradistinction to the “class I” behavior shown by Me_2Hg and Et_2Hg . Class II behavior was first found

TABLE VI
KINETIC PARAMETERS, Hg—C BONDS

Molecule	$\log_{10} \nu$ (sec ⁻¹)	Class	E_{act} (kcal/mole)	Reference
Me_2Hg	13.5	I	51.5 ± 2	(68, 96, 131)
	15.0	II?	57.9 ± 1.4	(145)
Et_2Hg	14.1	I	42.5 ± 2	(25)
Pr_2Hg	15.7	II	46.5	(30)
<i>i</i> - Pr_2Hg	16.4	II	40.7	(29)
	11 ± 2	I?	27 ± 5	(11)
Bu_2Hg	15.8	II	47.8	(11)
Vn_2Hg	11.9	I	48.3 ± 1	(172)
Ph_2Hg	16.0	II	68 ± 4	(25)
PhHgCl	13.0	I	59 ± 3	(25)
PhHgBr	14.3	I	63 ± 2	(25)
PhHgI	15.7	II	63 ± 2	(36)

by Chilton and Gowenlock (29, 30) in the pyrolysis of Pr_2Hg and $i\text{-Pr}_2\text{Hg}$, and led to the suggestion that in these cases the primary step determining the activation energy is the simultaneous rupture of *both* Hg—C bonds,



so that E_{act} should equal $(D_1 + D_2)$. The hypothesis of fission into three fragments was examined theoretically by Pritchard (134) in relation to the

TABLE VII
COMPARISON OF KINETIC AND THERMOCHEMICAL D VALUES OF Hg—C BONDS

Molecule	$(D_1 + D_2)$		D_1 Kinetic	D_2 By difference
	Thermo- chemical	Kinetic		
Me_2Hg	58.4 ± 2	57.9 ± 1.4	51.5 ± 2	6.9 ± 3
Et_2Hg	48.4 ± 4	—	42.5 ± 2	5.9 ± 4
Pr_2Hg	49 ± 4	46.5	—	—
$i\text{-Pr}_2\text{Hg}$	42 ± 4	40.7	27 ± 5	15 ± 7
Bu_2Hg	—	47.8	—	—
Vn_2Hg	$(67.4 \pm 6)^a$	—	48.3 ± 1	(19.1 ± 6)
Ph_2Hg	64.8 ± 4	68 ± 4	—	—
$\text{Hg}(\text{CN})_2$	144 ± 2	—	123 ± 7	23 ± 7

	$(D_1 + D_2)$		$D_1(\text{Ph—HgX})$	
	Thermo- chemical	Kinetic	Thermo- chemical	Kinetic
PhHgCl	90.4 ± 3	—	66.4 ± 3	59 ± 3
PhHgBr	$(80.6 \pm 4)^b$	—	(63.6 ± 4)	63 ± 2
PhHgI	$(69.6 \pm 4)^b$	63 ± 2	(61.6 ± 4)	—

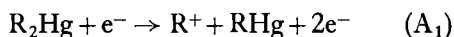
^a ΔH_f° (g) estimated by assuming the heat of hydrogenation is -30 ± 2 kcal per double bond per mole.

^b Assuming $\Delta H_g = 25 \pm 3$ kcal/mole.

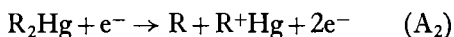
general rate equation for unimolecular decomposition; the mechanism was shown to be feasible and to lead to "high" frequency factors due to the accumulation of energy in several critical oscillators. The available kinetic parameters for mercury-carbon bonds, analyzed in accordance with these ideas, are summarized in Table VI, and compared with thermochemical deductions in Table VII.

The degree of agreement between kinetic and thermochemical D values

in Table VII is encouraging to the "multiple oscillators" theory, which however, remains to be established (146, 161, 162). To remove doubt further, Gowenlock *et al.* (67) turned to the electron impact method to provide independent confirmation of the kinetic results. Measurements of the appearance potentials of the ions R^+ and HgR^+ formed via the processes



and



were made on Me_2Hg , Et_2Hg , $i\text{-}Pr_2Hg$, and Bu_2Hg , from which $D_1(R-HgR)$ was derived through the relationships $D_1 \leq A_1 - I(R)$ and $D_1 \leq A_2 - I(HgR)$, where I = ionization potential. Unfortunately, the rupture process leading to R^+ ions appears to give considerable excess kinetic energy to the fragments and is not fruitful as a means of determining D_1 values. The alternative process, although less objectionable in this respect, is of limited value, due to uncertainty in the values available for $I(HgR)$. The D_1 values derived from A_2 (given in the table) are thus subject to rather wide error limits.

D_1	
Me_2Hg	60–75 kcal/mole
Et_2Hg	39–56 kcal/mole
$i\text{-}Pr_2Hg$	25–41 kcal/mole
Bu_2Hg	< 45 kcal/mole
$MeHgCl$	< 112 kcal/mole

The lower limits to D_1 for Et_2Hg and $i\text{-}Pr_2Hg$ are in fair agreement with the Class I activation energies. The electron impact values as a whole confirm the conclusion that $D_1 > D_2$.

The dissociation energies $D(R-HgX)$ can be obtained directly in the case of the methyl and ethyl mercuric halides ($X = Cl, Br, I$), as the required heats of formation, i.e., $\Delta H_f^\circ (RHgX, g)$, $\Delta H_f^\circ (R)$, and $\Delta H_f^\circ (HgX)$, are available; the values are as given.

$Me-HgCl = 64.3 \pm 2$	$Et-HgCl = 60.3 \pm 3$
$Me-HgBr = 61.8 \pm 2$	$Et-HgBr = 57.6 \pm 3$
$Me-HgI = 59.0 \pm 2$	$Et-HgI = 53.7 \pm 3$

It is noteworthy that the values $D(\text{R—HgX})$ are appreciably larger than $D(\text{R—HgR})$.

The pyrolysis kinetics of only a few metal alkyls, other than those of mercury, have been investigated. Most of these were carried out in static systems, giving complex kinetics of dubious value for bond energy purposes. Recent studies by Price and Trotman-Dickenson (131–133) using the toluene carrier gas flow technique have proved more rewarding, providing the tabulated values.

	D_1 (kcal/mole)
Me ₂ Zn	47.2 ± 1
	$D_2 = 35 \pm 5$
Me ₂ Cd	45.8 ± 1
Me ₃ Bi	44.0
Me ₃ Sb	57.0
Me ₂ SnCl ₂	56.1

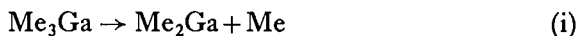
Combination of these data with the available thermochemical data gives the pattern of bond dissociation energies in the following tabulation.

	D_1	D_2
Me ₂ Zn	47.2 ± 1	36.8 ± 3 (thermo) 35 ± 5 (kinetic)
Me ₂ Cd	45.8 ± 1	20.8 ± 2 (thermo)
Me ₃ Bi	44.0	$(D_2 + D_3) = 58.3 \pm 4$ (thermo)
Me ₃ Sb	57.0	$(D_2 + D_3) = 97.5 \pm 5$ (thermo)
Me ₂ SnCl ₂	56.1	$D_2 = 30.3 \pm 4$ (thermo)

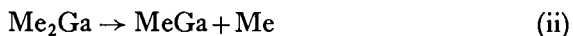
Thus it seems that $D_1 > D_2$ in zinc and cadmium alkyls, although less strongly so than in mercury alkyls, and that inequalities also apply to the D values in BiMe₃, SbMe₃, and Me₂SnCl₂. Price and Trotman-Dickenson (133) have tentatively deduced that $D_3 \leq 19.2$ kcal/mole in Me₃Bi; in this event, the thermochemistry requires $D_1 = 44$, $D_2 \geq 39$, $D_3 \leq 19$, i.e., $D_1 \neq D_2 \neq D_3$.

The pyrolysis kinetics of Me₃Ga were investigated by Jacko and Price

(84a) by the toluene flow method. Despite some complexities, it seems probable that the activation energies of the steps



and



should correspond closely with the dissociation energies, D_1 and D_2 . The kinetic data thus lead to $D_1 = 59.5$, and $D_2 = 35.4$ kcal/mole; since the thermochemistry requires $(D_1 + D_2 + D_3) = 177.2$ kcal/mole, it follows that $D_3 = 82.3$ kcal/mole. The pattern here is similar to that in Me_3Bi in that $D_1 \neq D_2 \neq D_3$, but quite different in that D_3 is the largest, not the smallest, of the individual D values.

Bond dissociation energies in a number of organoboron and organosilicon compounds have recently been reported by Steele *et al.* (163, 164) from electron impact studies. Measurements of the appearance potentials of the ions BF_2^+ and R^+ in RBF_2 ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, \text{vinyl}$), in conjunction with known (or estimated) ionization potentials, led to the tabulated values.

	D (kcal/mole)
Me— BF_2	95–100
Et— BF_2	101
<i>i</i> -Pr— BF_2	96
Vn— BF_2	111

In each case the values $D(\text{R—BF}_2)$ are substantially larger than $\bar{D}(\text{R—B})$ values in the corresponding boron alkyls. In like manner, from measurements of the appearance potentials of R^+ and SiH_3^+ in RSiH_3 ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}$), and of R^+ and SiCl_3^+ in RSiCl_3 , the dissociation energies were deduced.

Me— SiH_3	86 ± 4	Me— SiCl_3	93 ± 4
Et— SiH_3	89 ± 3	Et— SiCl_3	95 ± 4
<i>i</i> -Pr— SiH_3	79 ± 3	<i>i</i> -Pr— SiCl_3	80 ± 3
<i>t</i> -Bu— SiH_3	65 ± 3	<i>t</i> -Bu— SiCl_3	76 ± 3

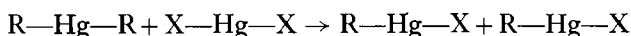
As pointed out by the authors, the nature of the electron impact method requires that these values be interpreted as *upper limits* to the individual bond energies. This may account in part for the large decrements in

$D(\text{R}-\text{SiH}_3)$, in passing from $\text{R} = \text{Et} \rightarrow i\text{-Pr} \rightarrow t\text{-Bu}$, and for the inconsistency in corresponding decrements in the series $D(\text{R}-\text{SiH}_3)$ and $D(\text{R}-\text{SiCl}_3)$.

VIII

REDISTRIBUTION REACTIONS OF METAL ALKYLs AND METAL HALIDES

Certain metal alkyls, MR_m , react with metal halides, MX_n , forming alkyl metal halides, e.g.,



In these "redistribution reactions" (150), no "new" bonds are formed, the reaction merely rearranging the bonds of the reactants. In terms of the simple hypothesis of constant, transferable bond energies, all gaseous redistribution reactions should be *thermoneutral*; in practice this is certainly not so for the redistribution reactions of alkyls of mercury and tin, some of which have been measured calorimetrically. In terms of the Allen bond energy scheme, these reactions will be exothermic provided

$$\Gamma_{\text{CMX}} > \frac{1}{2}(\Gamma_{\text{CMC}} + \Gamma_{\text{XMX}})$$

The available heats of redistribution, all of which are exothermic (some substantially so), are presented in Table VIII.

TABLE VIII
HEATS OF REDISTRIBUTION REACTIONS

Reaction	ΔH
$\frac{1}{2}\text{Me}_2\text{Hg} (\text{g}) + \frac{1}{2}\text{HgCl}_2 (\text{g}) \rightarrow \text{MeHgCl} (\text{g})$	-6.8
$\frac{1}{2}\text{Me}_2\text{Hg} (\text{g}) + \frac{1}{2}\text{HgBr}_2 (\text{g}) \rightarrow \text{MeHgBr} (\text{g})$	-5.2
$\frac{1}{2}\text{Me}_2\text{Hg} (\text{g}) + \frac{1}{2}\text{HgI}_2 (\text{g}) \rightarrow \text{MeHgI} (\text{g})$	-4.1
$\frac{1}{2}\text{Et}_2\text{Hg} (\text{g}) + \frac{1}{2}\text{HgCl}_2 (\text{g}) \rightarrow \text{EtHgCl} (\text{g})$	-7.7
$\frac{1}{2}\text{Et}_2\text{Hg} (\text{g}) + \frac{1}{2}\text{HgBr}_2 (\text{g}) \rightarrow \text{EtHgBr} (\text{g})$	-6.0
$\frac{1}{2}\text{Et}_2\text{Hg} (\text{g}) + \frac{1}{2}\text{HgI}_2 (\text{g}) \rightarrow \text{EtHgI} (\text{g})$	-3.8
$\frac{1}{2}\text{Ph}_2\text{Hg} (\text{g}) + \frac{1}{2}\text{HgCl}_2 (\text{g}) \rightarrow \text{PhHgCl} (\text{g})$	-5.6
$\frac{2}{3}\text{Bu}_3\text{B} (\text{g}) + \frac{1}{3}\text{BCl}_3 (\text{g}) \rightarrow \text{Bu}_2\text{BCl} (\text{g})$	-9.6
$\frac{2}{3}\text{Bu}_3\text{B} (\text{g}) + \frac{1}{3}\text{BBr}_3 (\text{g}) \rightarrow \text{Bu}_2\text{BBr} (\text{g})$	-9.8
$\frac{1}{3}\text{Me}_3\text{B} (\text{g}) + \frac{2}{3}\text{BF}_3 (\text{g}) \rightarrow \text{MeBF}_2 (\text{g})$	-9.1
$\frac{3}{4}\text{Me}_4\text{Sn} (\text{g}) + \frac{1}{4}\text{SnBr}_4 (\text{g}) \rightarrow \text{Me}_3\text{SnBr} (\text{g})$	-9.6
$\frac{3}{4}\text{Bu}_4\text{Sn} (\text{g}) + \frac{1}{4}\text{SnBr}_4 (\text{g}) \rightarrow \text{Bu}_3\text{SnBr} (\text{g})$	-5.3
$\frac{1}{2}\text{Me}_4\text{Sn} (\text{g}) + \frac{1}{2}\text{SnCl}_4 (\text{g}) \rightarrow \text{Me}_2\text{SnCl}_2 (\text{g})$	-7.0

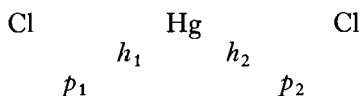
IX

INTRINSIC METAL-CARBON BOND ENERGIES

Intrinsic or "absolute" bond energies refer bond strength to the "valence states" of atoms in molecules; normally, the valence state will differ from the atomic ground state. The relevance of "intrinsic" bond strength becomes apparent when examining the stepwise dissociation energies, $D_1, D_2, \dots D_n$ in MX_n , each of which may differ from another.

The example of $HgCl_2$ ($D_1 = 81, D_2 = 24$) provides a good starting point for discussion. The molecule is linear in the gaseous state, and the $Hg-Cl$ bonds are equivalent. The bonding orbitals supplied by Hg are presumably equivalent linear hybrids, probably of type sp (deriving from $Hg, d^{10}sp, V_2$) which may be admixed to some extent with dp hybrids (from Hg, d^9s^2p, V_2). The V_2 valence state will include contributions from the atomic states of configuration $d^{10}sp$ (including 3P and 1P states, lying from 4.7–6.7 eV above the ground state, $6s^2, ^1S_0$) and perhaps from states of configuration d^9s^2p , the lowest of which lies 8.5 eV above the ground state. The promotion energy (124) required to attain the valence state, Hg, V_2 , is thus substantial, amounting to > 5 eV.

The approximate bonding energy of the four valence electrons in $HgCl_2$ may be written down by applying Mulliken's general formula (124), based on the valence-bond approximation of perfect pairing. Representing the structure $Cl-Hg^{II}-Cl$ in the manner



(p_1, p_2 are the Cl bonding orbitals, h_1, h_2 the Hg^{II} orbitals), the Mulliken formula gives:

$$\Delta H_a = X_{p_1 h_1} + X_{p_2 h_2} - \frac{1}{2} Y_{p_1 h_2} - \frac{1}{2} Y_{p_2 h_1} - \frac{1}{2} Y_{p_1 p_2} - P + RE \quad (9)$$

where X_{ij} is the "strength" of bond ij , Y_{kl} is the interaction between non-bonded orbitals k, l on different atoms, P the promotion energy to valence states, and RE the "resonance energy" of the molecule.

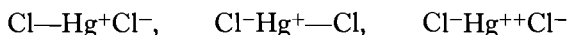
Writing

$$(X_{p_1 h_1} - \frac{1}{2} Y_{p_1 h_2}) = \epsilon_{Hg-Cl}$$

Eq. (9) may be recast as:

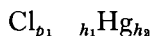
$$D_1 + D_2 = 2\epsilon_{Hg-Cl} - \frac{1}{2} Y_{p_1 p_2} - P + RE \quad (10)$$

where $\epsilon_{\text{Hg}-\text{Cl}}$ may be regarded as an effective "intrinsic" bond energy term in the ideal $\text{Cl}-\text{Hg}^{\text{II}}-\text{Cl}$ molecule. The value of P in Eq. (10) is the promotion energy to reach Hg, V_2 , h_1h_2 , and RE the resonance energy arising from the contribution to the bonding by ionic structures



and possibly by the "nonbonded" or "polarization" structure, $\text{Cl Hg}^\circ \text{Cl}$.

Turning to the radical $\cdot\text{HgCl}$, the formulation



leads to

$$\Delta H_a = D_2 = X_{p_1h_1}^* - \frac{1}{2}Y_{p_1h_2}^* - P^* + RE^* \quad (11)$$

or

$$D_2 = \epsilon_{\text{Hg}-\text{Cl}}^* - P^* + RE^* \quad (12)$$

The asterisks in (11) and (12) are included to allow for the possibility that the terms are numerically different from their values in (9) and (10). Mortimer (121) has pointed out that P^* is probably less than P , for whereas the hybrid orbitals h_1, h_2 in $\text{Cl}-\text{Hg}^{\text{II}}-\text{Cl}$ must be equivalent, this condition does not necessarily apply in $\cdot\text{Hg}-\text{Cl}$; Skinner (149) considered that the ionic contributions (per bond) to RE would probably differ in HgCl_2 and $\cdot\text{HgCl}$, and Gowanlock *et al.* (69) laid stress on the probable importance of "polarization" in weakly bonded HgX radicals (in particular, $\text{Hg}-\text{alkyl}$ radicals). The relationship between D_1 and D_2 , expressed by

$$(D_1 - D_2) = 2(\epsilon - \epsilon^*) - \frac{1}{2}Y + 2P^* - P + RE - 2RE^* \quad (11)$$

is not very helpful as it stands. However, it is probable that $P > P^*$ (121), and in the case of $\text{Hg}-\text{X}$ bonds which are not highly ionic one would expect $2RE^* > RE$ (69, 149); furthermore, if we assume that $\epsilon \sim \epsilon^*$, Eq. (11) reduces to

$$(D_1 - D_2) = P^* - \frac{1}{2}Y - dP - dRE \quad (12)$$

where $dP = P - P^*$, $dRE = 2RE^* - RE$.

Equation (12) provides for the experimental fact that $(D_1 - D_2)$ is generally decidedly less than the promotion energy required to attain the appropriate valence state, as Long (101) has emphasized.

Cotton *et al.* (32) have noted that although the \bar{D} values decrease along the series $\text{Ni}-\text{CO} \rightarrow \text{Cr}-\text{CO} \rightarrow \text{Fe}-\text{Co}$, the thermal stabilities of $\text{Fe}(\text{CO})_5 > \text{Cr}(\text{CO})_6 > \text{Ni}(\text{CO})_4$ increase, and suggest that this is because the intrinsic bond energies are higher in Fe and Cr carbonyls than in Ni carbonyl.

The excitation energies to reach the valence states Cr, V_0 , d^6 ; Fe, V_0 , d^8 ; and Ni, V_0 , d^{10} have been calculated (157) as 169, 153, and 42 kcal/gm atom, respectively; the mean bond dissociation energies *measured with respect to these valence states* are $\bar{D}^*(\text{Fe}-\text{CO}) = 58.6$, $\bar{D}^*(\text{Cr}-\text{CO}) = 57.7$, $\bar{D}^*(\text{Ni}-\text{CO}) = 45.7$ kcal/mole, reversing the order $\bar{D}(\text{Fe}-\text{CO}) = 28.0$, $\bar{D}(\text{Cr}-\text{CO}) = 29.5$, and $\bar{D}(\text{Ni}-\text{CO}) = 35.2$ kcal/mole, measured with respect to ground state atoms. This is only a partial explanation, however, since it now seems probable that the bond dissociation energy D_1 in nickel carbonyl is decidedly less than \bar{D} and \bar{D}^* . Kinetic studies by Basolo and Wojcicki (4a) of the exchange of radiocarbon monoxide, C^{14}O , with nickel carbonyl in toluene solution indicate an S_N1 process, $\text{Ni}(\text{CO})_4 \rightleftharpoons \text{Ni}(\text{CO})_3 + \text{CO}$, the activation energy for dissociation being only 13 kcal/mole. Moreover, whereas exchange is rapid with $\text{Ni}(\text{CO})_4$, it is very slow with $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$, confirming the order of the thermal stabilities.

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Electronic Structure of Alkali Metal Adducts of Aromatic Hydrocarbons

E. DE BOER

*Koninklijke/Shell-Laboratorium,
Amsterdam, Holland*

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I

INTRODUCTION

The reaction of alkali metals with aromatic hydrocarbons has been known for a long time. As early as 1867 Berthelot (1) reported that on fusing naphthalene with potassium in a closed tube a black addition product was

formed. This was the first of a long series of observations on this type of reaction to be reported. In this chapter an exhaustive survey of reactions of aromatic hydrocarbons with alkali metals will not be attempted; only the most important results of early studies will be mentioned. The stress will be on the better understanding of the properties and electronic nature of the reaction products gained in the course of the last two decades.

II

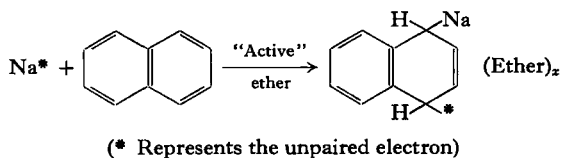
THEORIES OF CHEMICAL REDUCTION

A. Past Achievements

The oldest theory of chemical reduction stems from Baeyer (2). He supposed that the dissolved metals react with the solvent to liberate hydrogen atoms and that these hydrogen atoms *in statu nascendi* then react with the organic compound before they can combine with each other to form molecular hydrogen. The solvent plays a direct role in this theory.

Willstätter *et al.* (3) rejected the theory of "nascent" hydrogen, as a result of a careful study of the course of reductions by sodium amalgam. They proposed that sodium amalgam reductions start with the addition of metallic sodium to the double bond, the alkali metal being covalently bound to the carbon atom. If this reaction is followed by solvolysis, the attached alkali atoms will be replaced by hydrogen atoms. In this theory the solvent takes no direct part in the fundamental reaction.

Willstätter's theory has received considerable support from studies on the addition of alkali metals to olefins in inert media [Ziegler *et al.* (4-6) and Schlenk and Bergmann (7-11)]. Until recently, even the reaction between sodium and naphthalene has been formulated as (12-14).



In 1939 Hückel and Bretschneider (15) objected to Willstätter's theory as a general explanation. They pointed out that it is reasonable to assume that the mechanisms of reduction by alkali and by alkaline/earth metals are

the same. If Willstätter's explanation were correct a polyvalent atom such as Ca should add to the 1,4 position of naphthalene, which seems unlikely. Nevertheless naphthalene is reduced to the 1,4-dihydronaphthalene by both Na and Ca in liquid ammonia. Therefore Hückel and Bretschneider assumed a heteropolar structure for the compounds resulting from the addition of alkali metals to hydrocarbons. An electron is transferred from the alkali metal to the hydrocarbon. The electron added to the hydrocarbon they consider as localized on one carbon atom, to which the positive alkali ion is bound heteropolarly.

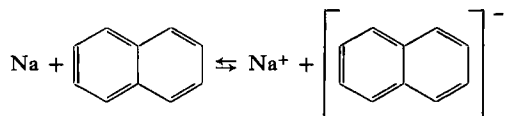
Evidence for the suggestion that the alkali adducts are ionic in character, is supplied by the experiments of Scott *et al.* (16). These authors observed a relatively high electrical conductance, but they paid no further attention to the structural implications of this observation.

B. Recent Developments

The recent progress in the determination of the structure of alkali-aromatics is characterized by a close coordination between experimental investigations and quantum mechanical theory.

The ionic behavior of the reaction products has been confirmed with various experimental techniques and it has been shown that mononegative as well as dinegative ions may be formed.

The existence of mononegative ions of aromatic hydrocarbons has been clearly demonstrated by the experiments of Lipkin *et al.* (17). These authors discussed the reaction of sodium metal with aromatic hydrocarbons in the presence of solvents such as 1,2-dimethoxyethane and tetrahydrofuran. They found that intensely colored solutions were formed, which exhibited strong paramagnetic resonance absorption, and concluded that free-radical ions were formed by the transfer of one electron to the aromatic compound. The reaction may be represented, using naphthalene as an example, by the equation



As already reported by Scott *et al.* (16) this reaction leads to an equilibrium. The value of the equilibrium constant will be determined chiefly by the magnitude of the energy of solvation of the ions. Solvents like methyl

ether or 1,2-dimethoxyethane are very favorable for solvation, whereas ethyl ether, for example, is relatively ineffective.

The electron spin resonance spectra of many aromatic univalent ions have been studied. They prove unambiguously that the added electron is not localized on a particular carbon atom, but is distributed over the whole molecule and forms an integral part of the delocalized π -electron system.

Polarographic reduction studies of aromatic hydrocarbons [Wawzonek *et al.* (18–21), Hoijsink *et al.* (22–27)] and potentiometric titration experiments (28) proved that besides mononegative ions, dinegative ions of aromatic hydrocarbons can also be formed. The polarographic current-potential curves showed in many instances two one-electron waves, indicating that the two following reactions occurred:

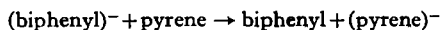


and



Reaction (2) took place at more negative potentials.

The potentiometric titration experiments illustrated this in another way. A standard solution of mononegative ions of biphenyl dissolved in 1,2-dimethoxyethane or tetrahydrofuran was added to solutions of aromatic hydrocarbons in the same solvent. As soon as the dark green standard solution came into contact with the solution of the hydrocarbon, for example pyrene, a rapid reaction took place, indicated by a color change from green to purple. Evidently an electron transfer occurred from the biphenyl anion to the neutral pyrene molecule.



When the reduction potential of the aromatic hydrocarbon is high enough a second electron may be transferred, involving the addition of an electron to the univalent negative ion. This is demonstrated in Fig. 1, which shows the photographic record obtained from the potentiometric titration of a solution of anthracene in tetrahydrofuran. Two successive waves appear, pointing to the occurrence of reactions (1) and (2), respectively.

The measurement of the electronic absorption spectra of the anions of aromatic hydrocarbons together with the interpretation given also contributed appreciably to a better understanding of the structure of the products of the reaction of alkali metals with hydrocarbons. The anions all give rise to a strong absorption in the visible range. On the basis of a quantum

mechanical description of the π -electron system the features of the spectra can be understood quite well (see Section V).

These developments of the last few years clearly indicate that reactions of aromatic hydrocarbons with alkali metals involve an electron transfer from the alkali metal to the hydrocarbon and may lead to uni- or divalent negative ions. The question of whether or not the ions can be considered as "free" solvated particles depends on the solvent and kind of alkali metal used.

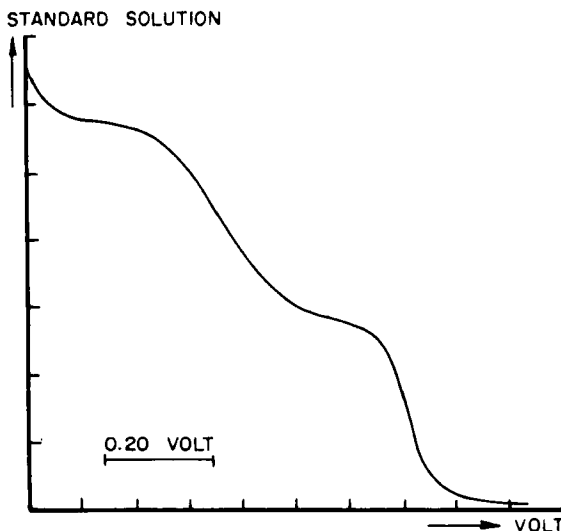


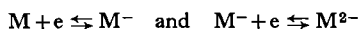
FIG. 1. Potentiometric titration of 0.01 *M* anthracene in tetrahydrofuran with standard solution; according to Hoijsink *et al.* (28).

III

ELECTRON AFFINITIES OF CONJUGATED HYDROCARBONS

A. Polarographic Measurements in Weakly Proton-Active Solvents

The polarographic reduction of aromatic hydrocarbons is a useful method for determining the electron affinities of conjugated hydrocarbons in solution. Investigations carried out in weakly proton-active solvents have shown that the reduction is governed by the following primary reactions (18-27):



The second reaction is slow, but the electron transfer step between M and M^- is very rapid.

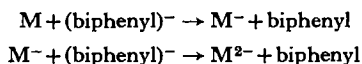
The rate constants of electron transfer between naphthalene and its anion are in the range 10^6 – 10^8 liter/mole sec, depending on solvent and alkali metal used (29, 30). The half-wave potential of the first electron addition step is therefore controlled almost solely by the Nernst equation and can be considered as approximately equal to the standard reduction potential. It will differ from it by $(RT/F)\ln(D_o/D_r)$, where D_o and D_r are the diffusion coefficients of the oxidized and reduced species, respectively. This term is normally of the order of a few millivolts.

The addition of a second electron is virtually irreversible, owing to the enhanced reactivity of the dinegative ions towards protons (31, 32). Another feature which influences the reduction potential of the second step more than the first step is the enhanced ability of dinegative ions to cluster with the positive counter ions. This renders the reduction potential of the univalent ion sensitive to the concentration and to the nature of the solvent, so that the second reduction potential cannot be considered as a standard potential. In Table I the reduction potentials of a number of conjugated hydrocarbons are compiled. From the table it appears that the difference, $\Delta\epsilon$, between the first and the second one-electron additions is of the order of a few tenths of a volt.

B. Potentiometric Titrations in Inert Solvents

The potentiometric titration experiments have provided information on the electron affinities in inert solvents, such as 1,2-dimethoxyethane or tetrahydrofuran (28).

In these experiments the dissolved hydrocarbons were titrated with a standard solution of biphenyl mononegative ions in the same solvent, so that the following reactions could occur:



It was found that for the standard solution in 1,2-dimethoxyethane, in which the initial concentration of biphenyl was 0.02 *M*, the reaction with sodium reaches an equilibrium at which the concentrations of biphenyl and univalent ion are about equal.

From the equilibrium condition in the solution,

$$(\epsilon_0)_{Na} + (RT/F) \ln [Na^+] = (\epsilon_0)_M + (RT/F) \ln \frac{[\text{biphenyl}]}{[(\text{biphenyl})^-]}$$

TABLE I

REDUCTION POTENTIALS OF CONJUGATED HYDROCARBONS AND THEIR MONONEGATIVE IONS IN A MIXTURE OF 96% DIOXANE AND 4% WATER

Hydrocarbon	$-\epsilon_{\frac{1}{2}}(M)^a$	$-\epsilon_{\frac{1}{2}}(M^-)^a$	$\Delta\epsilon_{\frac{1}{2}}$
Biphenyl	2.80	—	—
Naphthalene	2.60	—	—
Triphenylene	2.48	—	—
Phenanthrene	2.48	—	—
Terphenyl	2.41	—	—
Quaterphenyl	2.28	—	—
<i>trans</i> -1,2-Diphenylethene	2.22	—	—
1-Phenylbutadiene-1,3	2.17	—	—
Pyrene	2.10	—	—
1,2-Benzopyrene	2.10	2.49	+0.39
Coronene	2.05	2.44	+0.39
1,2,5,6-Dibenzanthracene	2.04	2.33	+0.29
1,2-Benzanthracene	2.00	2.35	+0.35
Anthracene	1.98	2.44	+0.46
3,4-Benzopyrene	1.84	2.18	+0.34
Fluoranthene	1.77	2.18	+0.41
Perylene	1.67	2.06	+0.39
Acenaphthylene	1.65	1.89	+0.24
Azulene	1.63	2.33	+0.60
Tetracene	1.58	1.93	+0.35
Decacyclene	1.49	1.84	+0.35
1-Phenyl-4-biphenylenebutadiene	1.45	1.68	+0.23
1-Phenyl-6-biphenylenehexatriene	1.35	1.55	+0.20
1-Phenyl-8-biphenyleneoctatetraene	1.29	1.45	+0.16
1,4-Dibiphenylenebutadiene	1.14	1.39	+0.25
Triphenylmethyl	1.05	—	—
1,2-Diphenylethene	2.22	—	—
1,4-Diphenylbutadiene	2.00	—	—
1,6-Diphenylhexatriene	1.85	—	—
1,8-Diphenyloctatetraene	1.71	—	—
1,10-Diphenyldecapentaene	1.63	—	—
1,12-Diphenyldodecahexaene	1.54	—	—

^a Expressed in volts with respect to the saturated calomel electrode; all data taken from ref. (27).

and the electron affinity of the hydrocarbon under investigation can rapidly provide a rough idea of the course of the reduction. With the aid of magnesium, for example, whose standard potential in aqueous solutions is about 1 volt more positive than that of sodium, anthracene cannot be converted into its ions, whereas dibiphenylene-ethene is easily reduced. A glance at Fig. 2 explains this at once.

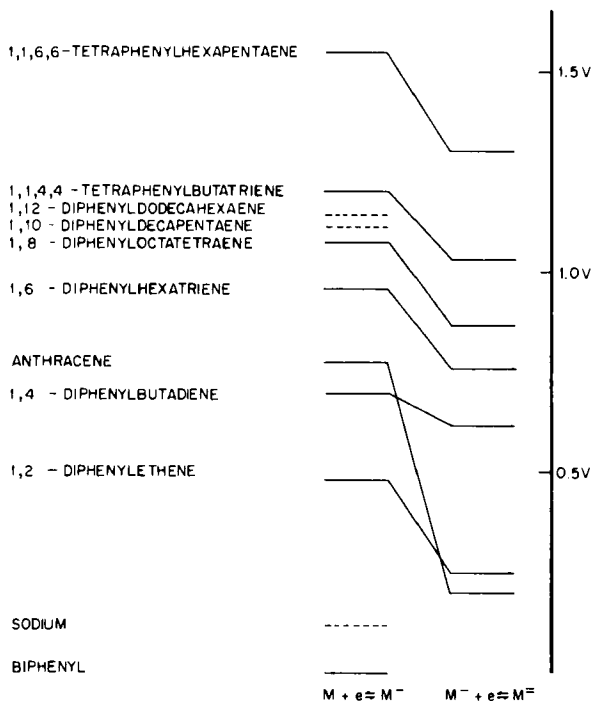


FIG. 3. The electrochemical series of some polyenes and cumulenes; according to van der Meij (56).

Matthias and Warhurst (34) report that the preparation of organic complexes of the alkaline earth metals Mg and Ca succeeded only with the aid of the amalgams of the metals. This may be caused by a lower ionization potential of the metal alloy as compared with that of its components.

C. Stability of Mononegative Ions to Disproportionation

In the gaseous state the difference in electron affinity between M and M^- is mainly due to the repulsion energy, ΔE_{rep} , between the two added

electrons in the lowest antibonding orbital of the dinegative ion (35). In order to calculate the energy, ΔE , of disproportionation of the univalent ions in solution:



the solvation energies of the ions must be known. Since the solvation energy of M^{2-} will be about four times that of M^- (see Born's equation), one can easily show that the difference in half-wave potential, $\Delta\epsilon$, is given by

$$F\Delta\epsilon = \Delta E_{\text{rep}} - 2(g_{M^-})_{\text{solv}}$$

where $(g_{M^-})_{\text{solv}}$ is the solvation free enthalpy of the mononegative ion and F is the Faraday constant. Hence the difference in reduction potential between the first and second reduction step results from a competition between electron repulsion and solvation energy. Both quantities are of the same order of magnitude (28, 35, 36), so that it is hard to predict the stability of the mononegative ion to disproportionation. The situation becomes even more complicated when strong ion association occurs. The difference, $\Delta\epsilon$, will then be diminished, since generally the dinegative ions are much more strongly associated with counter ions than the univalent ions.

The importance of this association effect is borne out by the results of Dieleman (37), who investigated the influence of temperature on the absorption spectra of sodium salt solutions of *p*-terphenyl negative ions and of *p,p'*-quaterphenyl negative ions in 2-methyltetrahydrofuran.

The unpublished results of an investigation in this laboratory (38) are a clear demonstration of the influence of this factor. In this investigation the absorption spectrum was measured of a solution obtained by reducing naphthalene, present at a concentration of $3.2 \times 10^{-3} M$ with lithium in 2-methyltetrahydrofuran at a temperature of -120°C . This spectrum, which is shown in Fig. 4, is identical with the spectrum of the mononegative ion of naphthalene (39). Elevation of the temperature of the solution introduces drastic changes in the spectrum; new bands arise, while simultaneously the bands due to the mononegative ion diminish in intensity. The dashed line in the figure represents the absorption spectrum at 0°C and corresponds to the situation where the bands of the univalent ion of naphthalene have vanished. A series of electron spin resonance measurements as a function of temperature revealed that these reversible optical changes were accompanied by a loss of paramagnetism. Evidently the enhanced associating power of the solution at higher temperatures causes disproportionation of the univalent ions into diamagnetic dinegative ions

and neutral molecules. The observed spectrum at 0°C is in agreement with the expected spectrum for a dinegative ion of a hydrocarbon belonging to the polyacenes (see Section V). The absorption bands of the formed neutral naphthalene molecules are not so clearly visible. The band which Clar (40) denotes by the symbol p (see Section V) is masked by the strong absorption band of the dinegative ion at 35,000 cm⁻¹. The irregular structure visible in the top of the latter band betrays its presence. The strong naphthalene

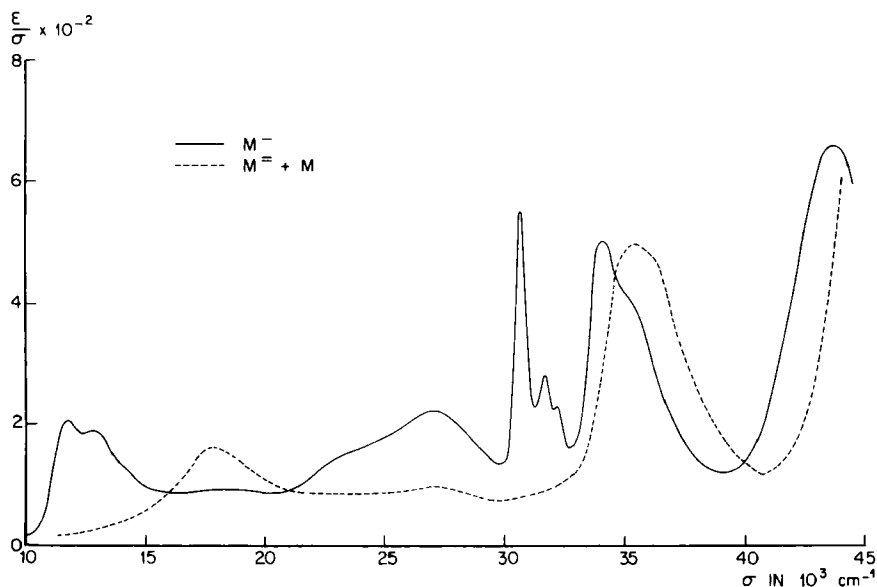


FIG. 4. Influence of the temperature on the absorption spectrum of the negative ions of naphthalene in 2-methyltetrahydrofuran with the positive ion of lithium as counter ion; solid line, -120°C; dashed line, 0°C.

band termed β^+ by Clar gives rise to the increasing absorption above 44,000 cm⁻¹.

The phenomena described here are strongly dependent on the solvent and the alkali metal. No disproportionation occurred in tetrahydrofuran and 1,2-dimethoxyethane, irrespective of the alkali metal used. The reaction of sodium or potassium with naphthalene in 2-methyltetrahydrofuran leads exclusively to the mononegative ion in the whole temperature range from -120° to +25°C.

In Table II the reduction potentials for a number of conjugated hydrocarbons, determined by potentiometric titrations, are given. If the $\Delta\epsilon$ values

are compared with those in Table I, it is apparent that in dimethoxyethane $\Delta\epsilon$ is increased. This is clearly illustrated by the series of the 1,*n*-diphenylpolyenes. In dimethoxyethane the two one-electron steps could be

TABLE II
REDUCTION POTENTIALS OF MOLECULES AND UNIVALENT ANIONS IN
1,2-DIMETHOXYETHANE^a

Hydrocarbon	ϵ_1^b	ϵ_2^b	$\Delta\epsilon$
Biphenyl	0.	—	—
Naphthalene	0.09	—	—
Phenanthrene	0.17	(0.05)	(0.1)
Triphenylene	0.19	—	—
Chrysene	0.38	—	—
1,2-Benzopyrene	0.58	—	—
Pyrene	0.60	—	—
1,2,5,6-Dibenzanthracene	0.69	0.14	0.55
Coronene	0.70	—	—
1,2-Benzanthracene	0.76	0.24	0.52
Anthracene	0.78	0.20	0.58
3,4-Benzopyrene	0.90	0.26	0.64
Fluoranthene	0.94	0.43	0.51
Perylene	1.09	0.46	0.63
Acenaphthylene	1.12	0.56	0.56
Tetracene	1.28	0.66	0.62
Dibiphenylene-ethene	1.59	1.20	0.39
1,2-Diphenylethene	0.48	0.25	0.23
1,4-Diphenylbutadiene	0.70	0.62	0.08
1,6-Diphenylhexatriene	0.96	0.76	0.20
1,8-Diphenyloctatetraene	1.08	0.87	0.21
1,10-Diphenyldecapentaene	(1.10)	—	—
1,12-Diphenyldodecahexaene	(1.14)	—	—

^a All data are taken from ref. (28) and (33).

^b Expressed against the standard potential of biphenyl.

distinguished separately; in a mixture of 96% dioxane and 4% water a single reduction wave appeared, corresponding to the uptake of two electrons. Apparently the stronger association in the mixture favors the formation of dinegative ions.

The difference $\Delta\epsilon$ determines whether or not the mononegative ions can be obtained substantially free from molecules and dinegative ions, say 99 % pure; $\Delta\epsilon$ must then be at least $2 \times 0.059 \log(99/1) = 0.24$ volt. Table II shows that according to this criterion it must be possible to obtain all mononegative ions comparatively pure with the exception of the diphenylbutadiene mononegative ion.

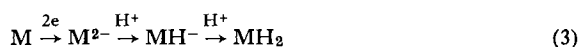
It has been confirmed spectroscopically that only with a tenfold excess of neutral molecules could the dinegative ion of diphenylbutadiene be converted into the univalent ion (33).

IV

THE COURSE OF THE CHEMICAL REDUCTION

A. Introductory Remarks

The recent advances in the understanding of the reaction of aromatic hydrocarbons with alkali metals have provided an explanation for many apparently unconnected experimental observations, such as those surveyed in 1942 by Campbell and Campbell (41) in a review article on the reduction and hydrogenation of molecules with multiple carbon-carbon bonds. A general approach to the course of chemical reduction, electrochemical reduction, and catalytic hydrogenation of hydrocarbons with conjugated double bonds has been given by Hoijtink (42-44). On the basis of the general reduction scheme



the course of the reduction and hydrogenation is predicted. It is assumed that the logarithm of the rate constant of proton addition to a particular carbon atom in the initially formed dinegative ion is proportional to the charge density at this carbon atom. Thus protonation will occur on the carbon atom carrying the highest negative charge.

Under the influence of electric fields arising from positive ions or from charged metal surfaces, the charge density may change considerably and consequently at high field strengths the proton may be added at another carbon atom. It is therefore desirable to distinguish between reductions in inert solvents and reductions in proton-active solvents.

B. Reduction in Inert Solvents

As has been pointed out, reduction of conjugated hydrocarbons in inert solvents may lead to mononegative or dinegative ions. On addition of a proton donor such as ethyl or methyl alcohol, protonation will occur at the carbon atoms having the highest negative charge. Since proton addition takes place in the bulk of the solution the effects of electric fields originating from the metal surface on the charge distribution can be neglected. The remaining effect of the fields of the positive ions is diminished by the strong solvation power of the added alcohol. Thus the charge distribution in the ions will hardly be disturbed by external factors and hydrogenation products whose structures are determined by the charge distributions in the unperturbed ions may be expected.

This is confirmed by the experimental results; reduction of phenanthrene, for example, with sodium in ether followed by hydrolysis leads to 9,10-dihydrophenanthrene. This is in agreement with the fact that the highest negative charge in the dinegative ion of phenanthrene is calculated to occur at the 9 and 10 positions.

C. Reduction in Proton-Active Solvents

In proton-active solvents the negative ions become protonated as soon as they are formed. Since protonation now takes place in the vicinity of the metal surface, polarizing effects on the negative hydrocarbon ion must be taken into account. Hoijsink has calculated the rate of proton addition for competitive carbon atoms in various dinegative ions as a function of the field strength. His results demonstrate that the structure of the final reduction products depends critically on the strength of the polarizing electric field. Referring to phenanthrene again it appears that at high field strengths the positions 1 and 8 have higher charge density than the positions 9 and 10. Accordingly, reduction of phenanthrene with sodium in alcohol leads to a mixture of 9,10-dihydro- and 1,2,3,4-tetrahydrophenanthrene. More extensive hydrogenation leads to the symmetrical and asymmetrical octahydrophenanthrenes (41) (see Fig. 5).

D. Properties of Protonated Anions

The properties of the ions MH^- primarily formed on protonation have been studied in detail for a number of aromatic hydrocarbons by Velthorst (45).

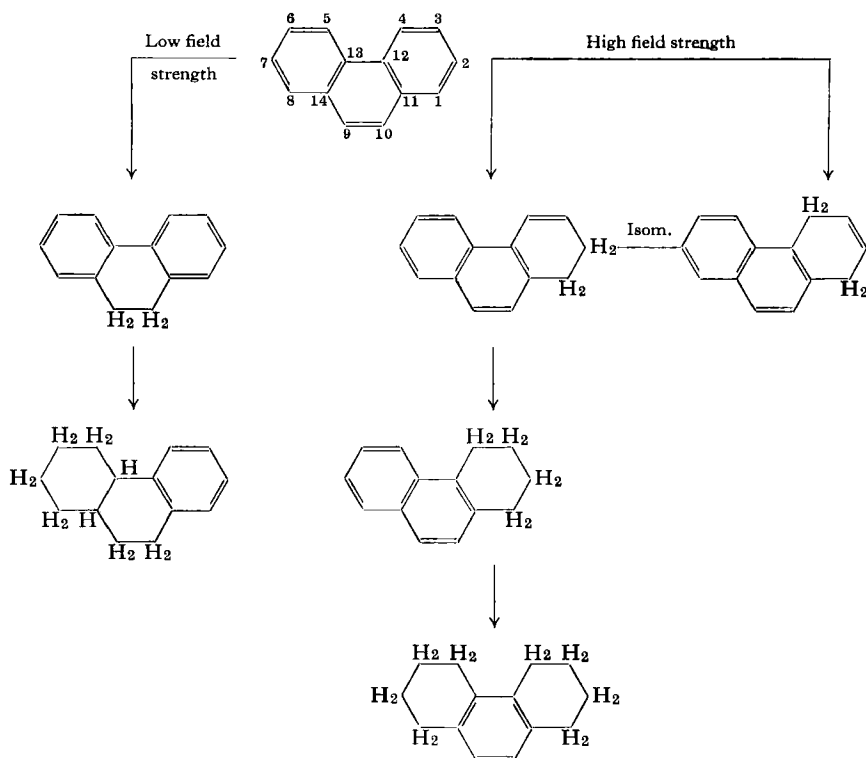


FIG. 5. Reduction scheme of phenanthrene; according to Hoijtink (43).

Since the structure of these ions is similar to the structure of the protonated aromatic hydrocarbons MH^+ (carbonium ions) we shall designate these negative ions as carbanions. The name negative ions will be reserved for hydrocarbon ions that differ from the parent compounds only by the presence of more electrons. The carbanions are obtained by means of the following reaction



Care must be taken that the reaction mixture does not come into contact with the alkali metal, otherwise the following reactions may occur.



When the dinegative ions cannot directly be formed with alkali metals, on account of the low position of the aromatic in the electrochemical scale

(Fig. 2) the carbanions can be obtained by starting from the mononegative ion and treating this with a proton donor, for example the nonvolatile stearyl alcohol. The reactions which then occur are



The initially formed radical MH has a much higher electron affinity than the original hydrocarbon molecule, so that the proton transfer is followed instantaneously by electron transfer, leading to a 1:1 mixture of hydrocarbon and its carbanion. The troublesome presence of neutral molecules

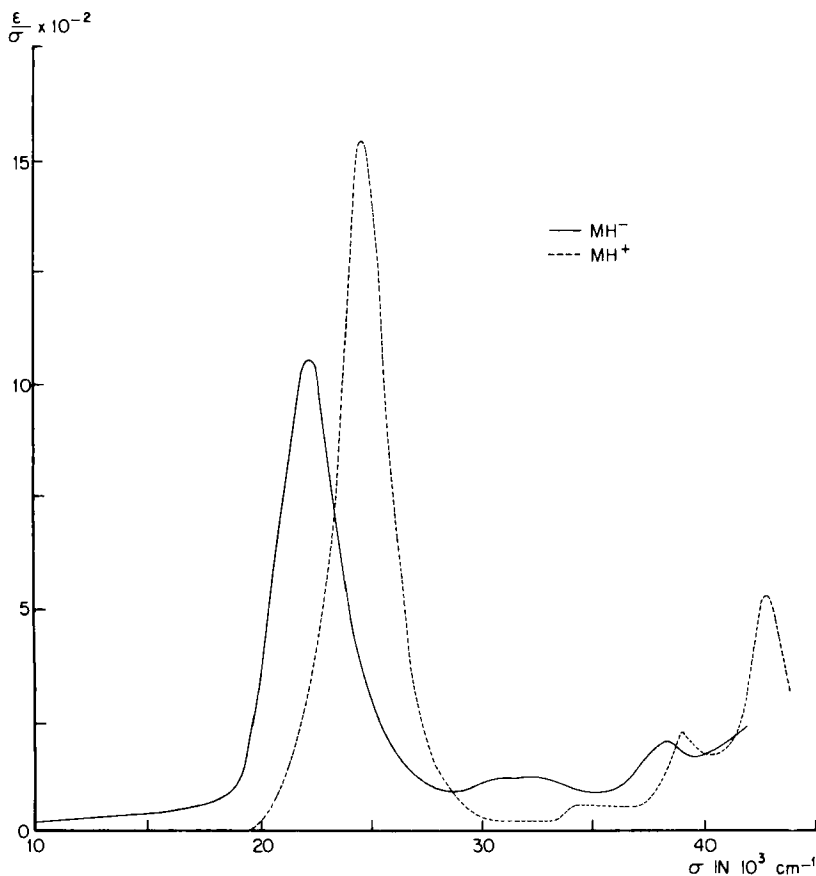
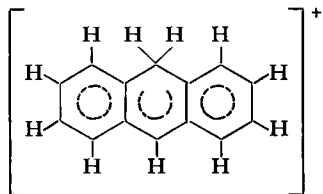


FIG. 6. The absorption spectra of the carbanion and the carbonium ion of anthracene; according to Velthorst (45).

can be avoided if the carbanions are stable towards the alkali metals. In this case reaction (5) can be applied.

The proton addition reaction to the negative ions of naphthalene, anthracene, tetracene, biphenyl, pyrene, perylene, and phenanthrene has been thoroughly investigated (45). Stable carbanions could be obtained from naphthalene, anthracene, and biphenyl. To elucidate the structure of the carbanions their electronic absorption spectra were studied. On theoretical grounds (46, 47) one may expect the spectra of carbanions MH^- and carbonium ions MH^+ with the same geometrical structure to be very similar. Mackor *et al.* (48, 49) have studied the spectra of a number of carbonium ions, so that a comparison could be made. In Fig. 6 the spectra of the anthracene carbonium ion and carbanion are shown; the similarity of the two spectra suggests that the ions have the same structure. The structure of the carbonium ion has been determined unambiguously by means of its nuclear magnetic resonance spectrum (50). It appeared that protonation occurred at the 9 position and that the carbonium ion has the following structure



One may conclude that in the carbanion the proton is also attached to the carbon atom in the 9 position. The slight shift of the absorption bands of MH^- with respect to the corresponding bands of MH^+ can be explained by the inductive effect of the aliphatic CH_2 group, which causes opposite changes in the excitation energies of corresponding transitions.

The experiments on tetracene revealed that the carbanion derived from it is not stable and disproportionates according to



An equilibrium mixture was obtained containing the species MH^- , MH_2 , and M^{2-} . Attempts to prepare stable carbanions of pyrene, perylene and phenanthrene did not succeed. Thermodynamic considerations make it apparent that the carbanions of these ions are very unstable and that the disproportionation reaction (10) is followed by electron transfer processes.

For phenanthrene the following equilibrium was established



and for pyrene and perylene even



Whether or not electron transfer processes occur after disproportionation depends on the electron affinity of MH_2 and MH_2^- with respect to M^- and M , respectively. It is predicted (45) that the reduction potentials ϵ_1 and ϵ_2 of 3,4-dihydropyrene and 2,3-dihydroperylene are higher than the reduction potentials ϵ_1 of the parent compounds, in agreement with the occurrence of reaction (12).

Reaction (11) may have to be taken into account in electron spin resonance studies of negative ions of aromatic hydrocarbons, using alkali metals as reducing agents. In the case of very reactive ions it is not always possible to prevent reactions of the ions with the solvent, so that small amounts of partly hydrogenated products are formed, which might disproportionate to paramagnetic hydrogenated ions according to reaction (11). If the possibility of such reactions is disregarded the electron spin resonance spectrum obtained may present puzzling features.

V

THE ELECTRONIC ABSORPTION SPECTRA OF NEGATIVE IONS

A. Introduction

The electronic spectra of the mono- and divalent negative ions in the 5,000–45,000 cm^{-1} region of various alternant aromatic hydrocarbons (51–55) and 1, n -diphenylpolyenes (56, 33) have been reported. The transitions observed in this spectral range are excitations within the delocalized π -electron system. Hoijsink *et al.* (57–61) have given a satisfactory explanation for the experimental results in relatively simple quantum-mechanical terms.

In a quantum-mechanical description of the delocalized π -electron system, the π electrons are described by orbital functions extending over the entire molecule. These orbitals are called molecular orbitals (MO's). In

most MO treatments the molecular orbitals are approximated as linear combinations of atomic $2p$ orbitals (LCAO-MO method). Each of the $2n$ carbon atoms in a conjugated hydrocarbon molecule contributes one π electron. From the $2n$ atomic $2p$ orbitals, $2n$ independent linear combinations can be formed and consequently a set of $2n$ molecular orbitals are obtained. To a first approximation each MO is associated with a certain orbital energy. According to Pauli's principle the n MO's with the lowest energies are each occupied in the ground state of the molecule by two π electrons with opposite spins. These orbitals are called the bonding orbitals. The remaining n unoccupied orbitals are called the antibonding orbitals.

The one-electron molecular orbitals and the corresponding orbital energies can be calculated with the aid of various approximation methods, e.g., that of Hückel (62, 63) or that of Pariser and Parr (64, 65). The most convenient starting point for the discussion of the π -electronic spectra of the anions are the Hückel one-electron molecular orbitals. These have the advantage that the same set of MO's can be used for both the molecule and its mono- and dinegative ion.

The discussion given here will be confined to alternant hydrocarbon anions, to which belong all condensed systems containing only even-membered rings. This class of compounds possesses certain unique features (66) within the Hückel and the Pariser and Parr approximations. One of the important properties is that the $2n$ π energy levels are symmetrically spaced on either side of the energy value which corresponds to the energy of a localized π electron in a $2p$ atomic orbital. Another feature is that the molecular orbitals are related to each other ("paired" orbitals) in such a way that if the n bonding orbitals are known, the n antibonding orbitals can easily be determined.

In the molecular orbital picture the ground states of the mono- and dinegative ions contain one and two electrons in the lowest antibonding orbital, respectively. Figure 7 is a schematic diagram of the energy levels of the π electrons in an alternant aromatic molecule and its anions. The dotted line in the figure represents the energy of a localized $2p$ π electron. The lowest antibonding orbital is denoted by $n+1$.

If one removes one or two electrons from the highest bonding orbital hydrocarbon cations are formed. This can be effected chemically by dissolving aromatic hydrocarbons in, for example, strongly oxidizing solvents (67-69). The electronic absorption spectra of positive and negative ions of the same hydrocarbon are strikingly similar, as will be noticed from the

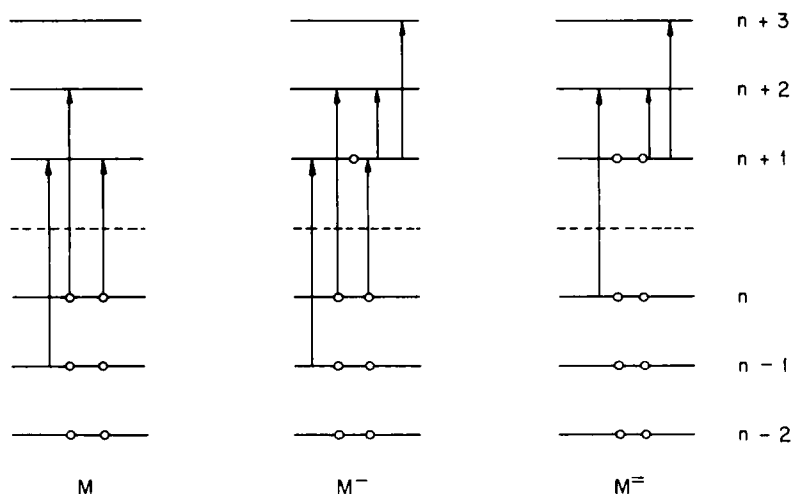


FIG. 7. The lowest principal electron excitations in alternant aromatic molecules and their mono- and dinegative ions.

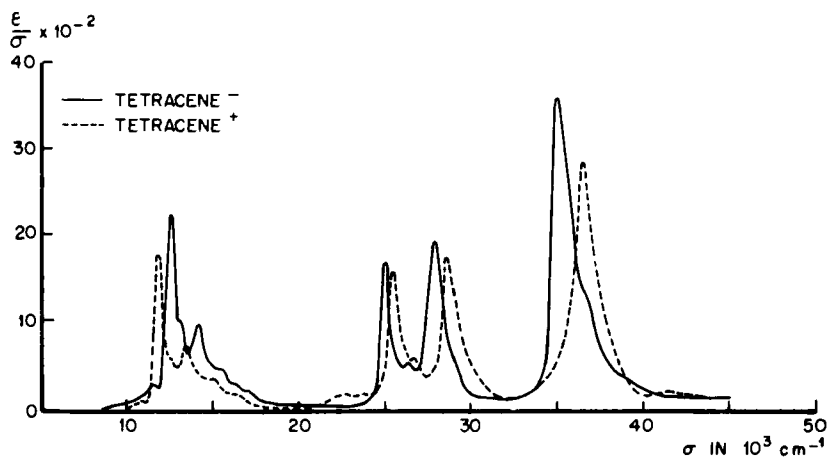


FIG. 8. The absorption spectra of the monovalent ions of tetracene; according to Weijland (55).

spectra of the mononegative and monopositive ion of tetracene, shown in Fig. 8. This similarity is due to the special relation which exists between the molecular orbitals of the positive and negative ions. On account of the existence of these relations it can be proved within the framework of the approximations used that the electronic absorption spectra of corresponding pairs of ions should be similar (55, 70). The interpretation given for the spectra of

the negative ions is therefore also valid for the absorption spectra of the positive ions (cf. Section IV, D).

In the following sections a brief discussion will be given of the characteristic features exhibited by the absorption spectra of alternant hydrocarbon molecules and their anions (cf. Fig. 7). In contrast with the solutions of the neutral hydrocarbons, the ionic solutions are all deeply colored. The transitions involving the orbital $n+1$, which give rise to absorption at long wavelengths, are responsible for this. Generally the absorption spectra of the dinegative ions are simpler than the spectra of the mononegative ions, on account of the doubly filled orbital $n+1$ in the former, so that the transitions $n+1 \leftarrow n-1$ and $n+1 \leftarrow n$ cannot take place.

B. The Neutral Molecule

If we restrict ourselves to the electron excitations giving rise to absorption of light in the visible and the near ultraviolet regions we need for the neutral molecule only to consider the excitations

$$n+1 \leftarrow n$$

$$n+1 \leftarrow n-1$$

$$n+2 \leftarrow n$$

Special attention has to be paid to the last two excitations, which to the approximation used here require equal energies. Therefore, the configurations corresponding to these two transitions are degenerate. Since the two configurations belong to the same symmetry class, the interaction energy between them will not necessarily be zero. From this it follows that the wave functions

$$\psi_{n+1 \leftarrow n-1} \quad \text{and} \quad \psi_{n+2 \leftarrow n}$$

of the two configurations are not the best wave functions for the description of the excited states. The best wave functions are obtained by taking the linear combinations

$$\psi_1 = 2^{-1/2}(\psi_{n+1 \leftarrow n-1} + \psi_{n+2 \leftarrow n})$$

$$\psi_2 = 2^{-1/2}(\psi_{n+1 \leftarrow n-1} - \psi_{n+2 \leftarrow n})$$

The energies associated with ψ_1 and ψ_2 are different, so that degeneracy no longer exists and two different states are obtained, designated by Pariser (65) as plus and minus states.

The experimental spectrum of alternant aromatic hydrocarbons will generally display a strong absorption band due to the transition to the plus state, a medium weak one due to the transition $n+1 \leftarrow n$, and a very weak one, since the transition to the minus state is formally forbidden. It should be noted that Clar (40) has introduced for the transition $n+1 \leftarrow n$ the symbol p and for the plus and minus states the notation β^+ and α .

The method for improving the wave function by taking linear combinations of functions obtained from the various electron configurations belonging to the same symmetry type has been called configuration interaction (65, 71, 72).

C. The Uni- and Divalent Negative Ions

Compared with the molecule, new transitions from the $(n+1)$ th level enter the term scheme of the mono- and dinegative ions. They are responsible for the main differences between the spectra of the molecules and the ions. The absorption band in the spectra of the ions that occurs at the longest wavelength originates from promotion of electrons in the lowest antibonding orbital $n+1$ to higher levels. Since in the dinegative ion the orbital $n+1$ is doubly filled, the dipole strength of transitions in the dinegative ions from the level $n+1$ to higher energy levels should be twice as strong as that of corresponding transitions in the univalent ions. In addition, the bands of the dinegative ion should be shifted to the blue with respect to the analogous bands of the mononegative ion, owing to repulsion between the two electrons in the dinegative ion. The experimental spectra reflect these features fairly clearly.

Besides these transitions, in the mononegative ion the transition $n+1 \leftarrow n$ is possible. Often this transition and the transition $n+2 \leftarrow n+1$ have parallel transition moments, so that configuration interaction will lead to two states described by a $+$ and a $-$ combination of the two separate configurations. This situation has been encountered in the spectra of the univalent ions of the 1, n -diphenylpolyenes (56, 33). Here the two excitations $n+1 \leftarrow n$ and $n+2 \leftarrow n+1$ have almost equal dipole strengths and excitation energies, so that a strong and a weak band will arise after configuration interaction has been included. Since all the other possible transitions in these ions have very low dipole strengths and occur at much higher frequency, the spectra of the mononegative ions should be characterized by these two bands only. The spectra of the dinegative ions should display one

strong band with an intensity about equal to the sum of the intensities of two bands in the spectra of the corresponding negative ions.

As an illustration Fig. 9 gives the spectra of the mono- and dinegative ion of 1,6-diphenylhexatriene (73). In the figure ϵ/σ has been plotted against σ so that the dipole strengths are directly proportional to the surfaces of the absorption bands.

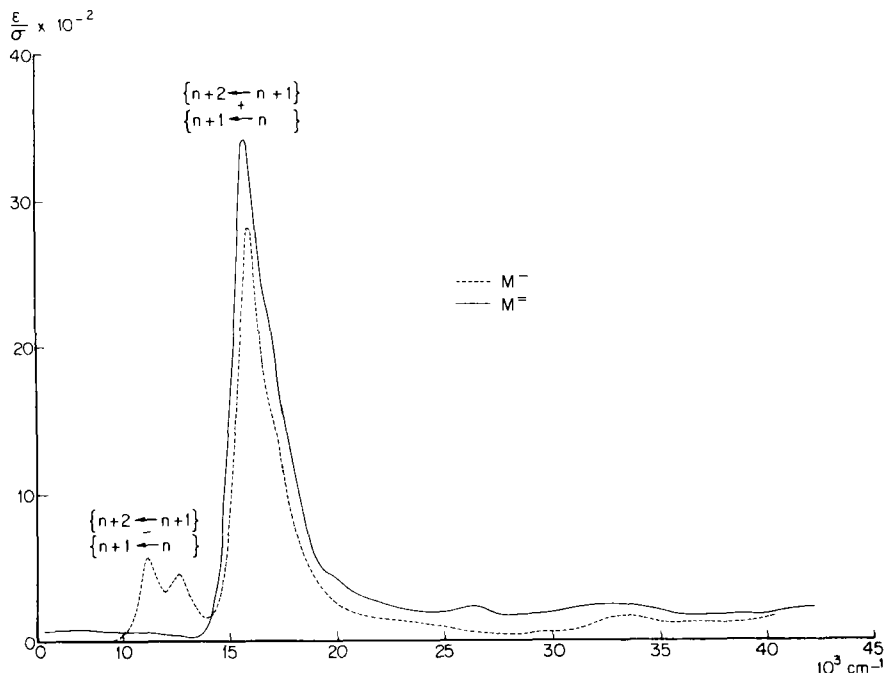


FIG. 9. The absorption spectra of the negative ions of 1,*n*-diphenylhexatriene: according to de Boer and van der Meij (73).

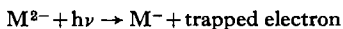
Concerning the other transitions the following remarks should be made. In the mononegative ion there are two transitions of about the same excitation energy, namely $n+2 \leftarrow n$ and $n+1 \leftarrow n-1$. The excitation $n+2 \leftarrow n$ leads to a configuration with three uncoupled spins, giving rise to two doublets and one quartet configuration (47). The excitation $n+1 \leftarrow n-1$ leads to one doublet configuration only. Since these three doublet configurations belong to the same symmetry type, they will interact and give rise to three excited states. Accordingly one may expect that the absorption spectra of the mononegative ions display three equally polarized absorption bands.

In the dinegative ion only the excitation $n + 2 \leftarrow n$ remains, which will result in one absorption band, with about half the intensity of the β^+ band of the molecule.

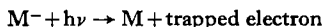
The absorption spectra of anthracene, as a typical representative of the series of the polyacenes, and of its anions are given in Fig. 10 (74). The symbols above the maxima of the absorption bands refer to the directions of polarization. The x -axis is taken along the longer axis of the molecule. The x -polarized absorption band located at about $13,000\text{ cm}^{-1}$ is due to the transition $n + 3 \leftarrow n + 1$ (the transition $n + 2 \leftarrow n + 1$ is symmetry forbidden). This same transition occurs in the dinegative ion, but it is shifted to the blue. The remaining three x -polarized bands in the spectrum of the mononegative ion originate from the excitations $n + 2 \leftarrow n$ and $n + 1 \leftarrow n - 1$. In the spectrum of the dinegative ion these three bands are replaced by one band, in agreement with the theoretical prediction.

D. Polarization Assignments

The interpretation of the absorption spectra of the negative ions of aromatic hydrocarbons is strongly supported by the polarization measurements of Hoijsink and Zandstra (39, 74, 75). They irradiated rigid solutions of various aromatic ions in 2-methyltetrahydrofuran with plane-polarized light of a wavelength corresponding to one of the ultraviolet absorption bands of the ions, and measured the directions of polarization of the electronic transitions. In this procedure, electrons are ejected from the negative ions according to the reactions



and



The product species formed will be distributed anisotropically, since the irradiation is most effective if the transition dipole moment of the original substance is parallel to the polarization direction of the irradiating beam. From absorption measurements on the irradiated solutions, using light whose plane of polarization is parallel and perpendicular to that of the exciting beam and with the same direction of propagation, the relative directions of polarization of the electronic transitions in the original and product substances can be measured. This method was first introduced by Lewis *et al.* (76, 77) who studied dichroism, in dyestuffs, induced by photoelectron ejection.

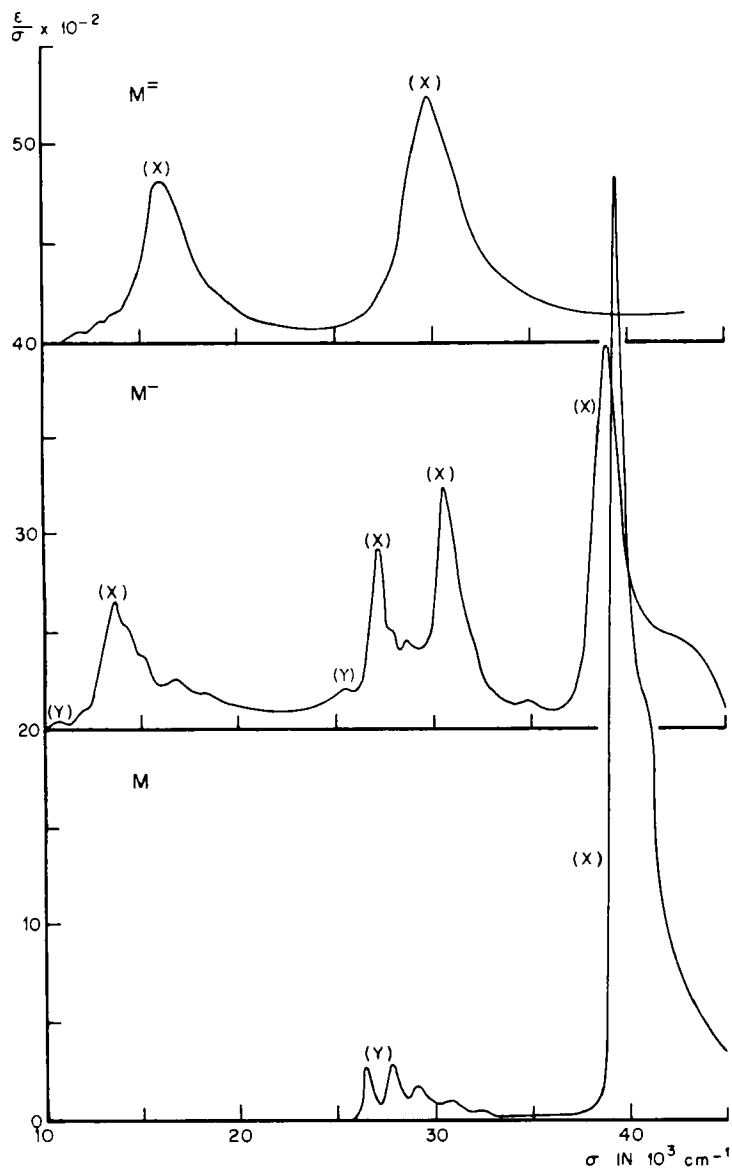


FIG. 10 Absorption spectra of the anthracene molecule and its ions; according to Hoijtink *et al.* (74).

The absolute assignments for the ions can be obtained only if the polarization of the absorption bands in the neutral molecule is known. Polarization measurements on single or mixed crystals have provided information on the latter (39). The polarization assignments indicated in Fig. 10 have been determined according to this method.

VI

THE ELECTRON DISTRIBUTION IN THE ANIONS

A. The Mononegative Ions with Doublet Ground State

Magnetic resonance measurements on the mononegative ions of hydrocarbons shed light on the unpaired electron distribution in the negative ions. This is clearly illustrated by the electron spin resonance spectrum of the mononegative ion of naphthalene. The resonance spectrum is not just a single line, but exhibits a remarkable fine structure (see Fig. 11). This fine structure arises from the interaction between the magnetic moments of the hydrogen nuclei in the molecule with the magnetic moment of the odd electron and is called hyperfine structure.

The hyperfine structure is described by the isotropic Fermi contact interaction term (78), which for the negative ion of naphthalene can be written in the form:

$$\mathcal{H}_{\text{hyperf}} = a_{\alpha} \vec{S} \cdot \vec{I}_{\alpha} + a_{\beta} \vec{S} \cdot \vec{I}_{\beta} \quad (13)$$

where S represents the electron spin, I_{α} the total nuclear spin of the four α protons, and I_{β} the total nuclear spin of the four β protons (measured in units of \hbar). The a 's in Eq. (13) are called the hyperfine interaction constants and are given by

$$a_{\text{H}} = (8\pi/3) g_{\text{e}} g_{\text{H}} \mu_{\beta} \mu_{\text{N}} [\psi(0)]_{\text{H}}^2 \quad (14)$$

where

- g_{e} = gyromagnetic ratio of electron;
- g_{H} = gyromagnetic ratio of proton;
- μ_{β} = Bohr magneton;
- μ_{N} = nuclear magneton;
- $\psi(0)$ = the amplitude of the wave function describing the odd electron at the position of the proton nucleus.

McConnell (79, 80) supposed that the hyperfine interaction constant a_{H} would be proportional to the fraction of an unpaired electron that was

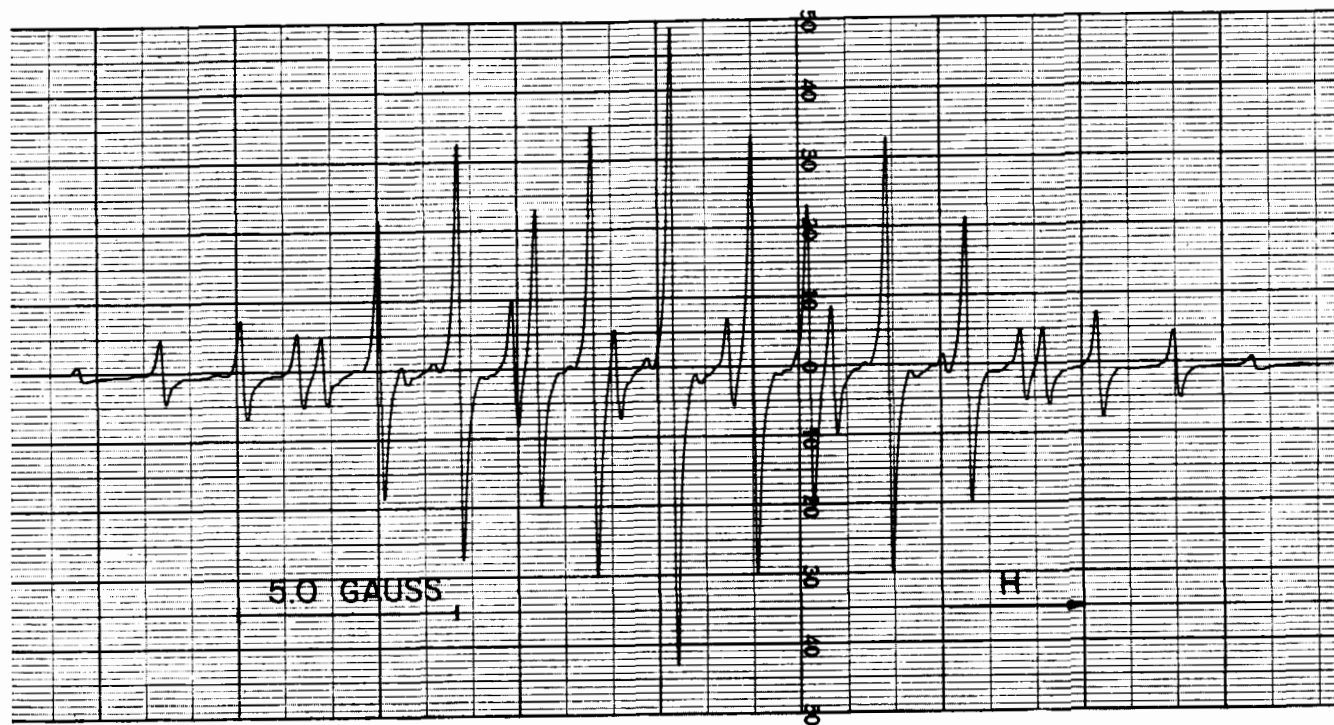


FIG. 11. The electron spin resonance spectrum of the naphthalene negative ion.

located in the $2p_z \pi$ orbital of the carbon atom to which the proton is attached and suggested the relationship

$$a_H = Q\rho_c^\pi \quad (15)$$

where ρ_c^π is the unpaired π electron spin density on the carbon atom and Q a proportionality constant. A value of Q in the neighborhood of -23 gauss is in good agreement with experiment.

This relation proved to be very useful. Since the splitting constant for the proton a_H follows directly from the intervals between the hyperfine components, relation (15) enables one to give a map of the spin distribution in the free radical. The magnitudes of the splitting constants observed for the negative ion of naphthalene are 4.95 and 1.865 gauss for the α and β protons, respectively (81). This gives for the ratios of the spin densities at the α and β position 2.65, which compares favorably with the theoretical spin density ratio of 2.62 calculated with Hückel's method.

Electron spin resonance spectra of the mononegative ions of various other aromatic hydrocarbons have been measured. Here too, the observed hyperfine splittings were in good agreement with the theoretically predicted spin densities (82-84).

B. The Dinegative Ions with Triplet Ground State

Usually the dinegative ions of aromatic hydrocarbons are in a singlet ground state and accordingly are diamagnetic (54). The dianions derived from molecules with a three- or sixfold axis of rotation may be exceptions. These molecules have the property that the highest bonding and the lowest antibonding π -electron levels are twofold degenerate. For this reason one may expect that the ground state of these dianions is a triplet. This has been confirmed for the dianions of decacyclene and 1,3,5-triphenylbenzene by means of electron spin resonance (85). These spectra were taken at liquid-nitrogen temperature in a rigid solvent since at room temperature no absorption is observed owing to strong spin-lattice relaxation (86). Similar experiments carried out for the dinegative ions of triphenylene and coronene have not yet led to definite conclusions regarding the multiplicity of the ground state.

Since the spectra of rigid solutions of randomly oriented paramagnetic species are superpositions of those corresponding to all orientations, the

hyperfine structure of each individual ion is masked and no detailed information is obtained concerning the distribution of the unpaired electrons over the molecule. However, the average distance between the two unpaired electrons emerges directly from the experimental spectra.

C. The Dinegative Ions with Singlet Ground State

Information on the total charge distribution in diamagnetic dinegative ions can be obtained by nuclear magnetic resonance measurements. Several investigators have shown that there is a definite correlation between proton chemical shifts and electronegativity. Corio and Dailey (87) investigated the effect of monosubstitution on the chemical shifts of the ring protons in benzene. They found that electron-withdrawing substituents cause a pronounced shift of the whole spectrum to low field with respect to benzene, whereas electron-donating substituents shift the whole spectrum to the high-field side of benzene. There seems to be no doubt that local charges have a most important effect on proton shifts and that these shifts can be taken as an approximate measure of electron density.

Studies have been made to establish the relation between chemical shifts and electron density. Theoretically a linear relation has been predicted between the shift and the excess π -charge density on the carbon atom to which the proton is attached (88, 89). The proportionality constant has been derived from nuclear magnetic resonance data provided by the ions C_5H_5^- , C_7H_7^+ , and $\text{C}_8\text{H}_8^{2-}$, in each of which the excess π -charge density on the carbon atoms is known.

A complicating factor is that the observed chemical shifts are not caused solely by the excess charge but are also influenced by "ring currents" induced in the aromatic rings and possibly by polar solvent and ion association effects. If corrections are made for these effects an approximate linear relation is found between the "observed" chemical shift, $\Delta\sigma$, and the excess electron density, Δq

$$\Delta\sigma = a \cdot \Delta q$$

For the proportionality factor a an average value of 9.3 ppm (parts per million) was obtained (90).

Many investigators have tried to correlate charge shifts and electron densities by using such a linear relation (91-94). In odd alternant ions

Colpa *et al.* found that the charge distribution measured by nuclear magnetic resonance is much more even than the calculated one, which shows rather large differences (93, 94). It must be realized, however, that the method measures the total charge on the carbon atom and not the π charge alone. Because of polarization of the σ electrons by the unevenly distributed π electrons, the total charge distribution should be more delocalized than the one calculated in a π electron approximation. Notwithstanding these additional complicating factors, nuclear magnetic resonance spectroscopy appears an attractive method for obtaining information on the charge distribution in dinegative ions.

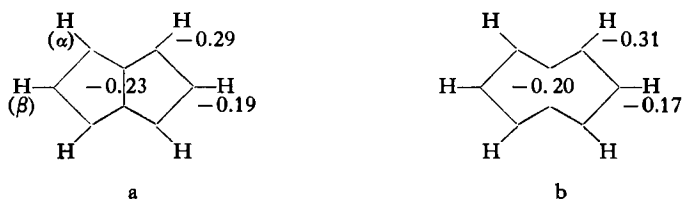


FIG. 12. Charge distribution in the pentalenyl di-anion (a) from nuclear magnetic resonance data, and (b) calculated according to Hückel.

An interesting example has been furnished by Katz and Rosenberger (95), who published the nuclear magnetic resonance spectrum of the pentalenyl dianion, the reduction product of pentalene, which is not known as the molecule. Using their experimental results and the dipole approximation for estimating contributions to the shielding due to ring currents (96) one calculates for the α and β protons charge shifts of 2.72 and 1.73 ppm, respectively. If we divide these values by 9.3, the charge distribution indicated in Fig. 12a is obtained. In Fig. 12b the π -charge distribution is given according to the simple Hückel method. The agreement between "observed" densities and calculated ones is satisfactory; here again the observed charge differences between the atoms are smaller than the calculated ones. An improvement would result if the polarization of the σ core by the π electrons were taken into account.

Finally it must be emphasized that the empirical relation between proton chemical shifts and charge densities is not so firmly established as the corresponding relation for the ESR hyperfine interaction constant (15). Many theoretical and experimental points remain to be clarified.

VII

THE NATURE OF ALKALI METAL-HYDROCARBON COMPLEXES IN SOLUTION

A. Introduction

The electronic absorption spectra of the aromatic alternant hydrocarbon anions have been interpreted under the assumption that the ions exist as "free" solvated particles in the solutions and accordingly no allowance has been made for the possible presence of cation effects. During the last few years evidence has been presented that such effects may induce marked changes in the spectra (37, 97-104). This has also been established by magnetic resonance investigations (81).

B. Ion-Pair Association Studied by Spectrophotometric Techniques

From their study of the reactions of organic halides with organosodium complexes in dioxane solution, Morantz and Warhurst (97) concluded that the measurements could be reconciled only with the concept of ion pairing. They concluded that the solutions contained exclusively the monomeric form of the radical anion paired with the alkali metal cation. The influence of the alkali ion on the electronic spectra was investigated by Carter *et al.* (100). They measured the absorption spectra in the region 10,000-25,000 cm^{-1} of a number of alkali metal complexes in dioxane solution and found that for a given radical anion the frequency of the maximum of an absorption peak shifted towards the red as the radius of the alkali metal cation increased. A relation was found between this frequency ν_m and the radius of the cation r_c

$$\nu_m \propto \frac{1}{r_c + 2}$$

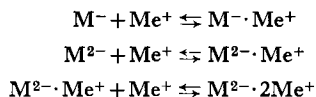
Using this relation, the maximum of the absorption band of the isolated solvated anion, which is of theoretical interest, was obtained by extrapolation ($r_c \rightarrow \infty$). The authors considered the complexes as contact ion pairs, consisting of a cation and an anion in close proximity and presumably surrounded by a solvation shell.

On the basis of the same model, McClelland (101) has given a theoretical

treatment of the electronic spectra of contact ion pairs constituted by an aromatic hydrocarbon anion containing a hetero (oxygen) atom and a positive alkali ion, using perturbation theory. He treats the effect of the alkali ion chiefly as a perturbation due to a charge $+e$ at its center and calculates the interaction energy for several positions of the cation with respect to the anion. In this way a surface in three dimensions can be constructed for the ground as well as for the excited state of the ion pair, which represents the variation in the energy of the ion pair when the cation moves in a plane parallel to the aromatic plane. If it is assumed that the transitions are vertical in accordance with the Frank-Condon principle, the vertical transitions between levels in the ion pair and those between the unperturbed levels of the "free" anion differ by an amount representing the change in the transition energy induced by the cation. Within the scope of this treatment the effect of the cation on an absorption band is determined entirely by the two molecular orbitals between which the transitions take place. If considerable mixing of energy levels occurs (in the case of degeneracy or near-degeneracy) a more sophisticated treatment is necessary.

The interaction energy curves for the ion pairs calculated along the lines indicated are quite shallow, which means that there will be thermal vibration of the cation about the minimum of the potential well. For the ions considered reasonable agreement is found with experimental data. The experimentally observed shift of the maximum of the longest wavelength band is in the predicted direction.

Aten *et al.* (104) have discussed ion-pair formation in relation to solvation, radius of the counter ion, and temperature in connection with a study of electron transfer reactions. According to Born's formula, which is qualitatively correct, the absolute value of the free enthalpy of solvation should increase with increasing dielectric constant and with decreasing radius of the ion. Because of the negative temperature coefficient of the dielectric constant the solvation should become stronger at lower temperatures. In accordance with these simple rules one expects formation of ion pairs to be favored by increasing radius of the metal ion and with decreasing dielectric constant (and consequently with increasing temperature). This is confirmed by the results of Dieleman and Hoijtink (37) on the influence of association on the electronic spectra of the negative ions of biphenyl, *p*-terphenyl, and *p,p'*-quaterphenyl dissolved in tetrahydrofuran or 2-methyltetrahydrofuran. Their measurements showed that the following concentration-dependent equilibria exist in the solution:



where M stands for the neutral molecule and Me for the alkali metal. Since the electronic spectra of the association products differ only slightly from

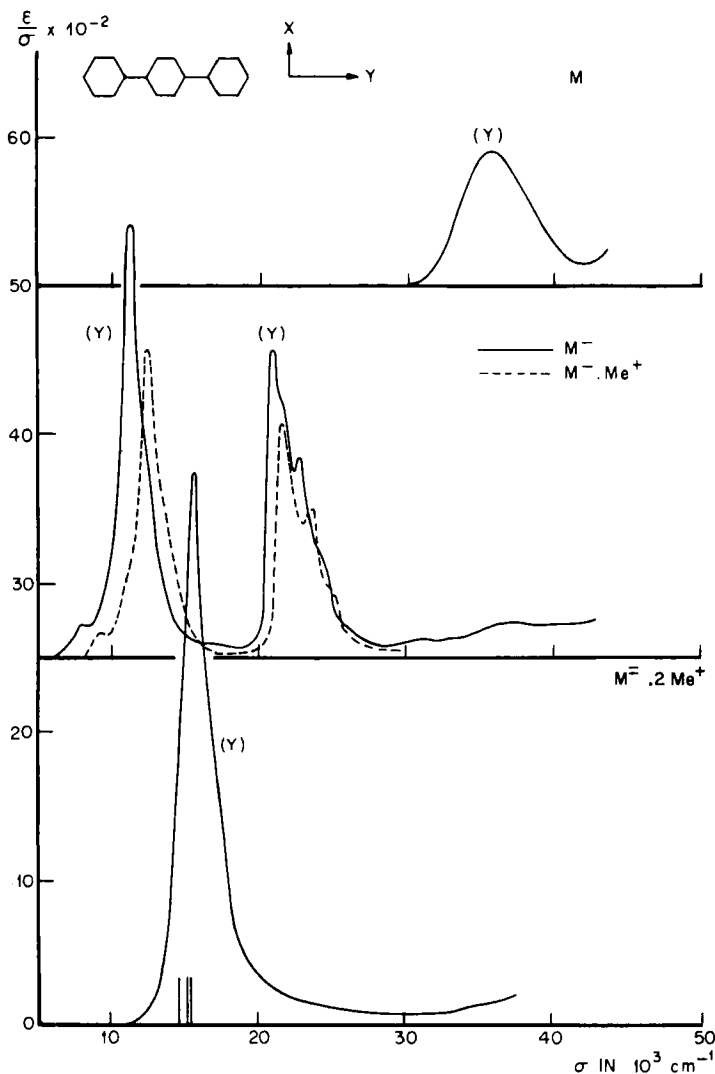


FIG. 13. Absorption spectra of the terphenyl molecule, the two forms of its mononegative ion, and one of the three forms of its dinegative ion; according to Dieleman (37)

those of the free solvated ions, the authors believe that the associates are of the solvent-shared type: a pair of ions linked electrostatically together by solvent molecules.

As an illustration, the electronic spectra of *p*-terphenyl, the two forms of its mononegative ion and one of the three forms of its dinegative ion, are given in Fig. 13. The vertical lines on the horizontal axis refer from left to right to the locations of the absorption maxima of M^{2-} , $M^{2-} \cdot Me^+$ and $M^{2-} \cdot 2Me^+$, respectively.

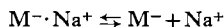
With the aid of a model similar to that used by McClelland the shifts in frequency and the changes in dipole strength of the absorption bands induced by the counter ion were calculated. The calculations revealed that the observed phenomena can only be accounted for if one layer of solvent molecules is present between positive and negative ions in these solvent-shared ion pairs. If this solvent layer is missing more drastic changes, such as the appearance of new bands not present in the spectrum of the "free" anion, are expected (105).

Recently Buschow and Hoijsink (105a) have investigated ion-pair formation with polyacene mono- and dinegative ions. Optical absorption spectra were measured of both the associated forms $M^- \cdot Me^+$, $M^{2-} \cdot 2Me^+$, $M^{2-} \cdot Me^+$, and the free solvated forms M^- and M^{2-} . Also, in this case the general form of the spectra of the associated forms is the same as that of the free solvated ions. The effect of the counter ions with respect to spectral changes becomes greater in the series K^+ , Na^+ , Li^+ . Quantum mechanical calculations proved useful in describing the two optical absorption spectra of M^- and M^{2-} and the effect of counter ions on them. The results suggest that the counter ions of the mononegative ions are situated at different positions from those of the dinegative ions and that the relative distance between the counter ion(s) and the negative ion is appreciably smaller in the case of the dinegative ion.

C. Ion Pairing Studied by Electron Spin Resonance

Direct evidence for the occurrence of ion pairs has been found by Atherton and Weissman (81). These authors measured the electron spin resonance spectrum of the negative ion of naphthalene in various solvents of low dielectric constant as a function of concentration and temperature. The association revealed itself by the occurrence of additional hyperfine lines, due to interaction of the unpaired electron with the spin (3/2) of the

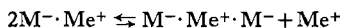
positive sodium ion. Under appropriate experimental conditions superposition spectra were obtained corresponding to the "free" ion and the associated form. By varying the temperature or the concentration the relative intensities of the two forms could be changed. The observed behavior could be accounted for by a simple dissociation process:



It is of interest to consider the thermodynamic quantities determined for this dissociation-association process. The equilibrium constant was estimated to be 1.74×10^{-6} mole/liter at 295.5°K in tetrahydrofuran with a total concentration of naphthalene of 1.33×10^{-4} mole/liter. From the temperature measurements it followed that $\Delta F^\circ = 7960$ cal, $\Delta H = -7500$ cal, and $\Delta S^\circ = -51.6$ e.u. A striking feature is the high negative value of the reaction entropy, probably characteristic for this type of process. Atherton and Weissman point out that this might arise from two causes reinforcing each other. The first one is that the sodium ion presumably finds itself in a very shallow potential well (see Section VII, B). Accordingly a high number of closely spaced vibrational states are accessible to it, which results in a large negative contribution to the entropy. The second entropy-decreasing factor is the solvation of the small sodium ion, which leads to some ordering of the solvent. These two factors combine so that the entropy ΔS becomes surprisingly strongly negative.

The observation of alkali metal hyperfine splitting implies a long-lived complex. Specifically the lifetime of the complex must be greater than or comparable to the reciprocal of the line width (expressed in frequency units). Since the total line width (usually 10^5 cps) will not entirely be due to the association-dissociation process, it is likely that each anion retains its sodium cation for a time of 10^{-5} second or longer.

Evidence for the formation of multiple ions has been found by Hirota and Weissman (106). These authors noticed that in alkali-fluorenone solutions ($10^{-4} M$) an equilibrium existed between the monomeric and the dimeric forms of similar electronic structure.



The dimeric form exhibited an electron spin resonance spectrum characteristic for species containing two unpaired electron spins. In addition to the $\Delta m = \pm 1$ transitions a transition was found at "half-field," corresponding to the $\Delta m = \pm 2$ transition (m refers to the total magnetic quantum number of the two electrons). This last transition is indicative for systems

in the triplet state (107, 108). Concentrated solutions of aromatic hydrocarbon anions ($10^{-1} M$) also show the "half-field" transition, pointing to formation of dimeric anion species (109).

A novel feature which shed some light on the structure of ion pairs has been observed by de Boer and Mackor (110, 111) for the negative ion of pyracene. In 2-methyltetrahydrofuran strong ion association occurs; over the whole temperature range studied, from 160° to $270^{\circ} K$, the electron spin resonance spectrum corresponded to the associated form and no traces of splitting due to the "free" anion could be detected. Analysis of the spectrum revealed that the eight aliphatic protons are no longer equivalent. This was ascribed to the close vicinity of the counter ion which causes changes in the

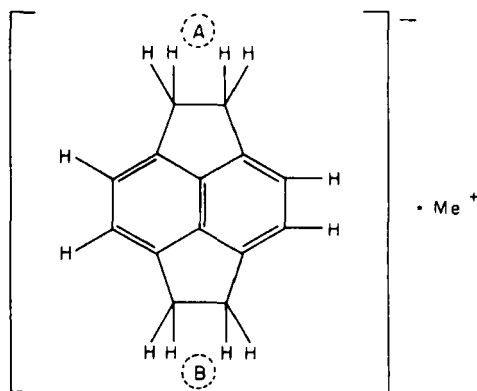
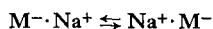


FIG. 14. Structure diagram for the alkali-radical ion complex of pyracene.

spin distribution. The location of the counter ion must be such that two sets of four equivalent protons arise. Furthermore it must account for the temperature dependency of the alkali splitting (which decreases at lower temperature) and for the fact that the value of the sodium splitting is much smaller in the pyracene complex than in the naphthalene ion pair. Taking all these factors into account, the most likely equilibrium positions of the cation are positions A and B in Fig. 14.

The electron spin resonance spectrum of the radical ion complex of pyracene in tetrahydrofuran (Fig. 15) revealed that the structure of the complex is dynamic in nature. A marked line-width alternation is observed (112-114), which arises from a dynamic equilibrium existing between the two possible conformations of the ion pair with the counter ion in position A and in position B.



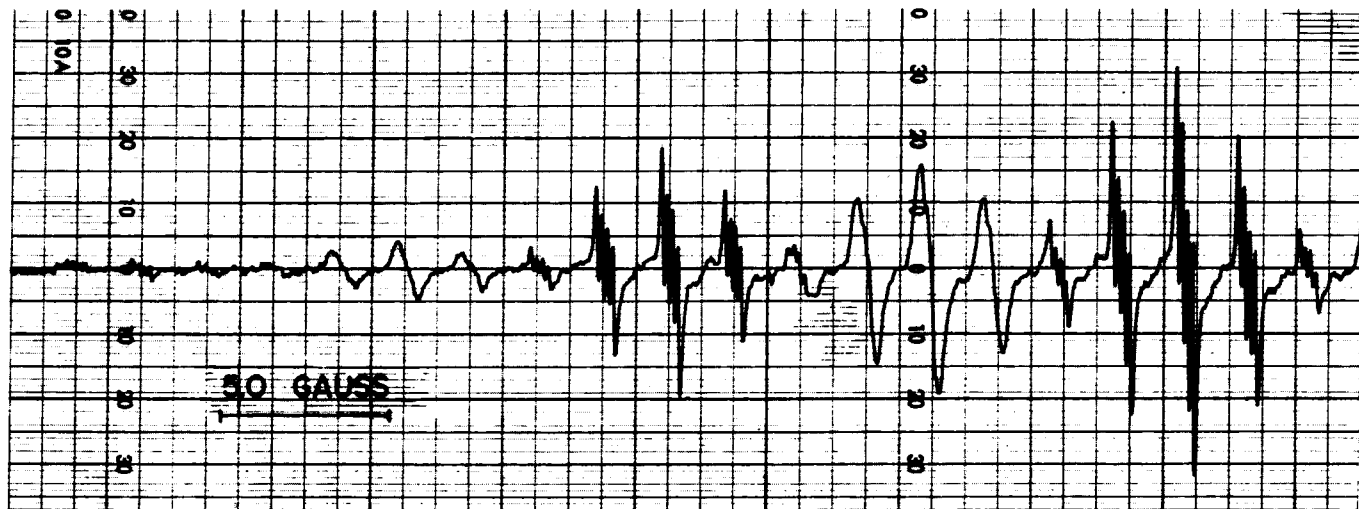


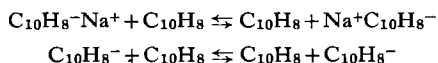
FIG. 15. Part of the electron spin resonance spectrum of the potassium-pyrene complex in tetrahydrofuran at -30°C .

The counter ion switches intramolecularly between the two symmetrical positions (A and B) with a frequency of the order of 10^7 – 10^8 cps. This means that the lifetime of a particular conformation of the ion pair is shorter than 10^{-7} second.

The switching frequency depends on the solvent: In 2-methyltetrahydrofuran at -80°C the rate is slower than 10^5 cps, while in tetrahydrofuran at -30°C the rate is faster than 10^7 cps. In the latter case many conformation changes occur within the lifetime of the ion pair, the cation switching back and forth between positions A and B.

In view of the features demonstrated by the solutions of the alkali-pyrene complexes one may expect similar phenomena to take place in other alkali-hydrocarbon systems. A dynamic picture of the ion pair would probably be a better representation of the real situation than a static one.

The effects of ion association on rates of electron transfer reactions have been studied by Zandstra and Weissman (115) for the sodium-naphthalene system. The following reactions were considered.



Generally, it was found that the transfer process involving the ion pair is slower than the one involving the dissociated ion. In the former case the electron transfer process is accompanied by a simultaneous transfer of the sodium ion.

Adam and Weissman (116, 117) found for a similar reaction occurring in the sodium-benzophenone system that the mean lifetime of the sodium ion in the ion pair is more than a thousand times greater than the mean lifetime of its counterpart in the ion pair complex, the benzophenone anion. For this reason this process has been called "atom transfer."

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Reactions of Alkali Metal Derivatives of Metal Carbonyls and Related Compounds

R. B. KING

*Mellon Institute, Pittsburgh,
Pennsylvania*

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I

INTRODUCTION

Metal carbonyls have been known for over 70 years. Within the last 35 years derivatives of the anions of the metal carbonyls have been synthesized. Within the last 10 years various derivatives of the metal carbonyl anions have acquired significance as intermediates in the preparation of interesting organometallic derivatives of the transition metals. In this chapter applications of anions derived from the metal carbonyls and the substituted metal carbonyls in syntheses of unusual organometallic derivatives of transition metals and the chemistry of the organometallic derivatives thus synthesized will be discussed.

Because the most synthetically useful anionic metal carbonyl derivatives are those of the alkali metals, the chemistry of this class of substances will be emphasized. These materials are often prepared from the free or amalgamated alkali metal and an appropriate metal carbonyl derivative in an ether or other inert aprotic solvent. The metal ammine and related salts of metal carbonyl anions, thoroughly studied by Hieber and co-workers in Munich over the last 15 years, will be treated in less detail since they are less useful synthetically. For a more detailed description of these compounds the reader is referred to the review article by Hieber *et al.* (1).

The organometallic compounds prepared from alkali metal derivatives of metal carbonyls include compounds in which a transition metal of a metal carbonyl residue is σ -bonded to another atom such as a carbon atom in an alkyl, acyl, aryl, or perfluoroalkyl group, to the heavier congeners of carbon—silicon, germanium, tin, and lead—to mercury and gold which form unusually stable compounds, and even to other transition metals. The preparation and properties of all of these classes of compounds will be considered and, for the sake of completeness, a few related compounds prepared by routes other than those involving anionic metal carbonyl derivatives will be discussed.

In Table I a portion of the periodic table is presented with an indication as to the elements forming neutral “pure” metal carbonyls (those containing only carbon monoxide bonded to a metal atom), (designated as P°); the elements forming neutral “mixed” metal carbonyl derivatives (those containing ligands other than carbon monoxide such as halogen or cyclopentadienyl), (designated as M°); the elements forming anionic “pure” metal carbonyl derivatives (designated as P^-), and the elements forming anionic

TABLE I
METALS WHICH FORM CARBONYL DERIVATIVES^a

Ti	V		Cr		Mn		Fe		Co		Ni		Cu
M°	P°	M°	P°	M°	P°	M°	P°	M°	P°	M°	P°	M°	M°
	P ⁻	M ⁻	P ⁻	M ⁻	P ⁻	M ⁻	P ⁻	M ⁻	P ⁻	M ⁻	P ⁻	M ⁻	
	[V(CO) ₆] ⁻		[C ₅ H ₅ Cr(CO) ₃] ⁻		[Mn(CO) ₅] ⁻		[C ₅ H ₅ Fe(CO) ₂] ⁻ [Fe(CO) ₄] ²⁻		[Co(CO) ₄] ⁻				
Zr	Nb		Mo		Tc		Ru		Rh		Pd		Ag
	M°		P°		P°		P°		P°		M°		
	P ⁻		P ⁻		P ⁻		M ⁻						
			[C ₅ H ₅ Mo(CO) ₃] ⁻		[Tc(CO) ₅] ⁻		[C ₅ H ₅ Ru(CO) ₂] ⁻						
Hf	Ta		W		Re		Os		Ir		Pt		Au
	M°		P°		P°		P°		P°		M°		M°
	P ⁻		P ⁻		P ⁻								
			[C ₅ H ₅ W(CO) ₃] ⁻		[Re(CO) ₅] ⁻								

^a P°—Metal forms neutral carbonyl derivative(s) with only carbon monoxide as ligands.

P⁻—Metal forms anionic carbonyl derivative(s) with only carbon monoxide as ligands.

M°—Metal forms neutral carbonyl derivative(s) containing ligands other than carbon monoxide.

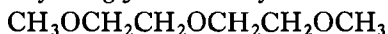
M⁻—Metal forms anionic carbonyl derivative(s) containing ligands other than carbon monoxide.

“mixed” metal carbonyl derivatives (designated as M^-). Anions playing a particularly important role in the chemistry to be discussed in this chapter are also indicated on the periodic table.

List of Abbreviations

In order to save space many of the organic ligands will be designated by commonly used abbreviations such as the following:

diglyme = *diethylene glycol dimethyl ether*:



o-phen = *o*-phenanthroline: $\text{C}_{12}\text{H}_8\text{N}_2$

bipy = 2,2'-bipyridine (α, α' -dipyridyl): $\text{C}_{10}\text{H}_8\text{N}_2$

en = ethylenediamine: $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

py = pyridine: $\text{C}_5\text{H}_5\text{N}$

Tdp = tris(dimethylamino)phosphine: $[(\text{CH}_3)_2\text{N}]_3\text{P}$

In addition, certain categories of groups or elements will be designated by special abbreviations such as the following:

R = all types of organic radicals (alkyl, aryl, etc.) σ -bonded to another species

R_f = perfluoroalkyl radical

X = chlorine, bromine, iodine, and occasionally fluorine (halogens)

Ck = sulfur, selenium, tellurium (chalcogens)

Pn = phosphorus, arsenic, antimony, and occasionally nitrogen and bismuth (“pnigogens”)

M, M' = metals of various types (especially transition metals and alkali metals)

E = elements of a specified type for which the above abbreviations are not particularly suitable, especially silicon, germanium, tin, and lead.

Unless otherwise specified organic radicals designated as C_3H_7 , C_4H_9 , C_5H_{11} , etc., will refer to the straight chain (“normal”) isomers. The designation C_6H_5 will refer to the phenyl group and the designations C_5H_5 , C_6H_6 , and C_7H_7 to the π -bonded cyclopentadienyl, benzene, and cycloheptatrienyl rings, respectively.

II

PREPARATION OF ANIONIC METAL CARBONYL DERIVATIVES

Methods suitable for the preparation of alkali metal and other salts of carbonyl anions may be divided into three categories:

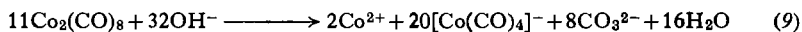
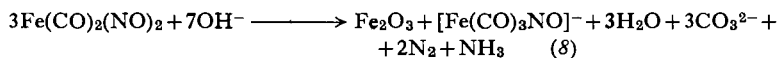
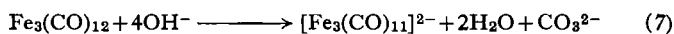
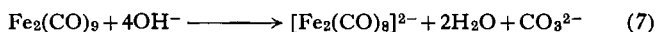
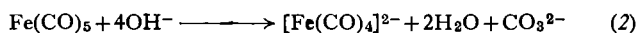
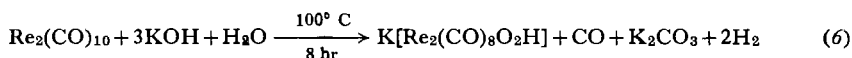
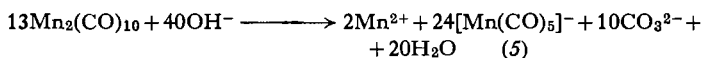
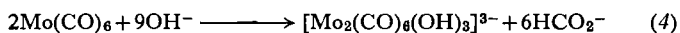
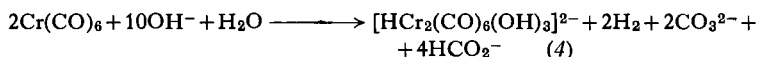
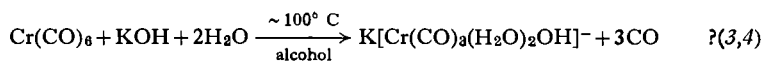
(1) reaction of a metal carbonyl derivative with bases such as hydroxide ion, isocyanides, or derivatives of trivalent nitrogen, phosphorus, arsenic or antimony;

(2) reaction of a metal carbonyl derivative with reducing agents such as alkali metals or complex hydrides;

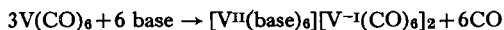
(3) substitution of carbon monoxide in a metal carbonyl derivative by an anion, thus producing a substituted anionic metal carbonyl derivative.

A. Metal Carbonyls and Bases

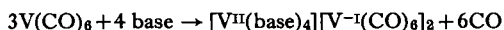
This is the earliest method used for the preparation of alkali metal and other derivatives of metal carbonyl anions. In 1931 the reaction between iron pentacarbonyl and aqueous hydroxide ion to give the $[\text{Fe}(\text{CO})_4]^{2-}$ anion was first described (2). Since that time the reactions between hydroxide ion and various metal carbonyl derivatives have been used to prepare a variety of anions, as illustrated by the following equations.



The related reactions between Lewis bases, especially amines, and various metal carbonyl derivatives have been utilized largely by Hieber and co-workers to prepare a variety of metal carbonyl anions. Examples of reactions of this type are illustrated by the following equations:



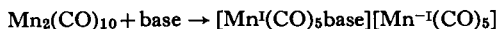
base = aniline (10), *N,N'*-diphenylethylenediamine (10), *o*- and *p*-phenylenediamine (10), acetonitrile (10), benzonitrile (10), acetone (11), acetophenone (11), methanol (11), cyclohexanone (11), 1/2 benzil (11), tetrahydrofuran (11), morpholine (11), formylmorpholine (11), dimethylformamide (11), benzamide (11), etc.



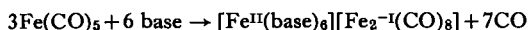
base = α - or γ -picoline (10), benzophenone (11), dioxane (11), dimethyl ether (11), ethyl acetate (11), triphenylphosphinemethylene (11), triphenylphosphineimine (11), triphenylarsine oxide (11), etc.



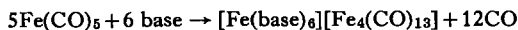
base = pyridine (12), γ -picoline (13), diethanolamine (13), morpholine (13), 1/2 ethylenediamine (13), 1/3 diethylenetriamine (13), piperidine (13), 1/2 2,2'-bipyridyl (13)



base = *n*-butylamine (13)



base = ammonia [in the presence of hydroxylamine (14) or pyridine (15)], *o*-phenanthroline (16)



base = pyridine (17), dimethylsulfoxide (18), piperidine [with concomitant formylation of the base to formylpiperidine (19)], *o*-phenanthroline (16)



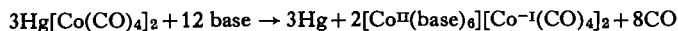
base = 1/2 ethylenediamine (20)



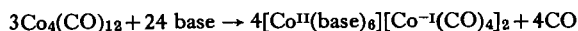
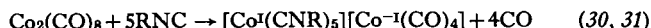
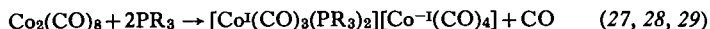
base = pyridine *N*-oxide (18), pyridine (17)



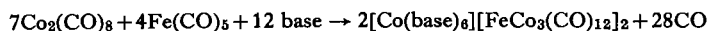
base = ammonia (21, 22, 24), pyridine (23, 24), 1/2 ethylenediamine (24), methanol (24), ethanol (24), water (24), *o*-phenanthroline (24), acetonitrile (24), aniline (24), acetamide (24), acetone (24), tetrahydrofuran (24), methylamine (24), dimethylamine (24), piperidine (24), α - and γ -picoline (25), quinoline (25), pyrrolidine (25), morpholine (25), ethyleneimine (25), formamide (25), Schiff bases (25), diacetylanil (25), 1/3 diethylenetriamine (25), diethanolamine (25), triethanolamine (25), acetonitrile (25), benzonitrile (25), acetophenone (25), benzophenone (25), benzil (25), etc.



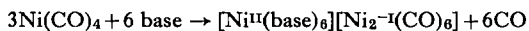
base = pyridine (26)



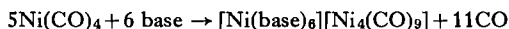
base = ammonia (21, 22)



base = acetone (32)



base = 1/2 *o*-phenanthroline (33), pyridine (in the presence of OH⁻) (33), amines (33)



base = 1/2 ethylenediamine (in the presence of pyridine) (33)

This method of generating anionic metal carbonyl derivatives by reaction of metal carbonyl derivatives with Lewis bases has the following disadvantages:

(1) *Loss of metal.* Even if the conversion from the metal carbonyl derivative to the anionic metal carbonyl is quantitative, a significant percentage of the metal in the original metal carbonyl derivative (20–50 %) is lost as a complex cation due to the stoichiometry of the reaction.

(2) *Interference by Lewis base.* The presence of a Lewis base in the system may interfere with the use of the anionic metal carbonyl derivative for reaction with another reagent. For example, the presence of pyridine would interfere with the reaction of a metal carbonyl with methyl iodide or acetyl chloride; even the presence of methanol would interfere with the reaction between an anionic metal carbonyl derivative and acetyl chloride. If the salt of the metal carbonyl anion is isolated in the pure state, the presence of relatively weakly bonded, coordinated Lewis-base molecules in a cation, such as $[\text{Mn}(\text{base})_6]^{2+}$ or $[\text{Fe}(\text{base})_6]^{2+}$, may interfere in a similar manner.

For these reasons the reactions between metal carbonyls and Lewis bases are not frequently used when the resulting carbonyl anion is desired for a further reaction. Therefore, the reactions between metal carbonyl derivatives and Lewis bases to prepare anionic metal carbonyls are emphasized less in this article than other preparative methods.

$[\text{FeCo}_3(\text{CO})_{12}]^-$ is the only anion presently known which cannot be prepared without using a Lewis base. Sometimes, as in the case of $[\text{Co}(\text{CO})_3(\text{PR}_3)_2]^+$, the cation formed in the reaction between a metal carbonyl derivative and a Lewis base is of interest, for there is no other method of preparation.

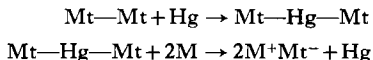
B. Metal Carbonyls and Reducing Agents

The most useful method for obtaining anionic metal carbonyl derivatives for preparative purposes is the reduction of various metal carbonyls with an alkali metal or amalgam, generally in the presence of a basic solvent such as liquid ammonia or various ethers. In order to minimize formation of metal

carbonyl anions by the reaction of the metal carbonyl with the solvent alone, with concomitant loss of some of the metal as the cation $[M(\text{solvent})_6]^{2+}$, it is desirable to use a solvent which is a sufficiently weak base for this reaction to be negligible. It is also desirable to use a solvent which will not react with the halide or other material to be reacted later with the metal carbonyl anion.

One frequently used solvent for the alkali metal reduction of metal carbonyls is liquid ammonia, in which alkali metals form blue solutions. These blue solutions are useful for some of the more drastic reductions, such as that of the very stable octahedral chromium hexacarbonyl to the anion $[\text{Cr}(\text{CO})_5]^{2-}$. Unfortunately, the reactivity of liquid ammonia toward most of the halide derivatives of interest for reaction with metal carbonyl anions has seriously limited its use in their preparation. Behrens and co-workers, however, have made an extensive study of the reactions of the $[\text{Cr}(\text{CO})_5]^{2-}$ anion prepared by the reduction of chromium hexacarbonyl with sodium metal in liquid ammonia; these reactions will be discussed later.

The use of relatively inert ethers such as tetrahydrofuran or diethyl ether as solvents in the reduction of metal carbonyls to anions with alkali metals has fewer disadvantages. Unfortunately, sodium and lithium metals, the most readily available and conveniently handled alkali metals, are not soluble in ethers. Blue solutions, similar to those obtained from alkali metals in liquid ammonia, may be obtained from the liquid sodium-potassium eutectic in tetrahydrofuran (34), but the inconvenience and hazards of handling this very reactive liquid alloy have limited the uses of this reagent. Instead, the most commonly used reducing agent in tetrahydrofuran or diethyl ether solution has been a very dilute liquid ($\sim 1\%$) sodium amalgam. The liquid nature of this amalgam prevents the reaction from being stopped by the formation of a crust on the surface of the metal. In addition, the mercury may be a catalyst in the formation of an alkali metal derivative by this reaction. The mechanism involves the formation of an intermediate mercury derivative HgMt_2 and cleavage of this mercury derivative with the alkali metal, e.g.



where Mt = a univalent metal carbonyl radical such as $-\text{Co}(\text{CO})_4$, $-\text{Mn}(\text{CO})_5$, $-\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$, $-\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$, etc.; and M = an alkali metal such as sodium or lithium). This hypothesis is supported by the recent isolation of mercury derivatives of this type from sodium amalgam reduc-

tions of metal carbonyl derivatives (34, 35, 36) and by the reaction of dicobalt octacarbonyl with mercury to give $\text{Hg}[\text{Co}(\text{CO})_4]_2$ (37).

Sometimes mercury derivatives formed in the preparation of alkali metal carbonyls by reduction with sodium amalgam are potential contaminants in metal carbonyl derivatives prepared from the resulting sodium compounds. Moreover, in large-scale preparations the quantity of mercury required for the dilute amalgams can be very large and thus inconvenient. It is possible to avoid the presence of mercury in reductions of metal carbonyls such as $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$ by the use of lithium wire in tetrahydrofuran (38).

Reduction by alkali metals for the preparation of anionic metal carbonyl derivatives is illustrated by the following equations.



M = sodium amalgam (ethanol or benzene) (10, 39)



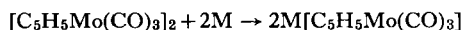
M = sodium (liquid ammonia) (40)



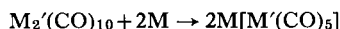
M' = Cr, Mo, and W; M = sodium (41), lithium (41), calcium (41), barium (41), (liquid ammonia); M' = Cr; M = sodium amalgam (boiling tetrahydrofuran) (42)



M = sodium (liquid ammonia) (43)



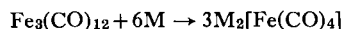
M = sodium (tetrahydrofuran) (44); also carried out for analogous alkylcyclopentadienyl derivatives (44)



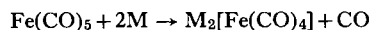
M' = Mn, M = sodium amalgam (tetrahydrofuran) (5); M' = Mn, M = lithium (tetrahydrofuran) (38); M' = Tc, M = sodium amalgam (tetrahydrofuran) (45); M' = Re, M = sodium (46, 47) or lithium (46) amalgams (tetrahydrofuran or dimethyl ether)



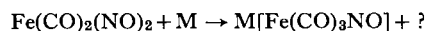
R = phenyl, ethyl, cyclohexyl, or phenoxy; M = sodium, lithium, or magnesium amalgams (tetrahydrofuran or dimethyl ether) (48, 49)



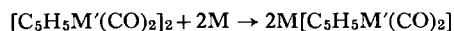
M = sodium or sodium amalgam (tetrahydrofuran) (50); M = sodium (liquid ammonia) (21)



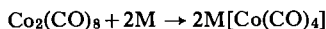
M = sodium (liquid ammonia) (21)



M = sodium amalgam (tetrahydrofuran) (8)

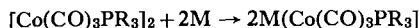


M' = Fe, M = sodium amalgam [methanol (51) or tetrahydrofuran (52)]; M' = Ru, M = sodium amalgam (tetrahydrofuran) (53)



M = sodium amalgam (benzene (54), diethyl ether (55), or dimethyl ether (55);

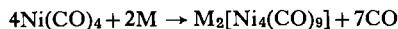
M = lithium (tetrahydrofuran) (38)



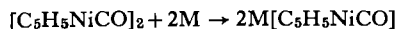
R = phenyl or phenoxy; M = sodium amalgam (tetrahydrofuran) (56, 57)



M = alkali or alkaline earth metals (liquid ammonia) (58, 59)

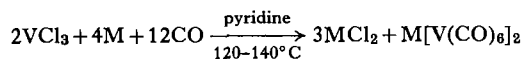


M = sodium amalgam (tetrahydrofuran) (33)

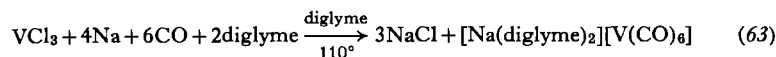


M = potassium amalgam (tetrahydrofuran) (60)

Somewhat related to these reactions is the preparation of the hexacarbonylvanadate(− I) anion by the carbonylation of vanadium(III) chloride in the presence of an active metal and a basic solvent

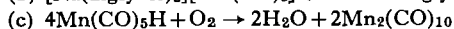
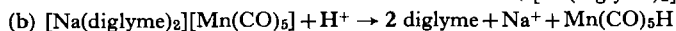
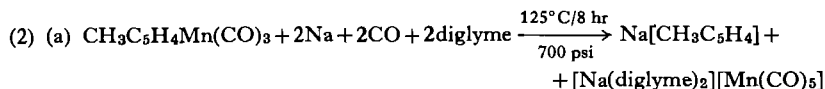
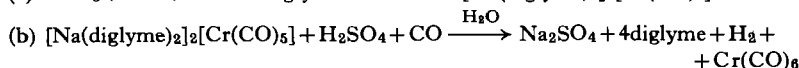
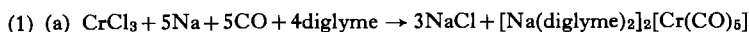


M = magnesium-zinc mixture (61, 62)



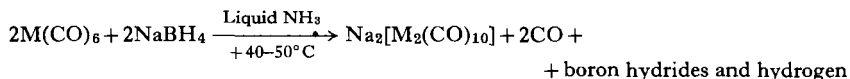
The second method is useful for preparing large quantities of vanadium carbonyl derivatives.

An analogous reaction carried out on niobium and tantalum pentachlorides is reported to give the carbonyl derivatives $[\text{Na}(\text{diglyme})_2][\text{M}(\text{CO})_6]$ (M = Nb, Ta) (63). Similar formation of a sodium derivative of a metal carbonyl as an intermediate may also occur in the following preparations of chromium (42) and manganese (64) carbonyls with elemental sodium as the reducing agent

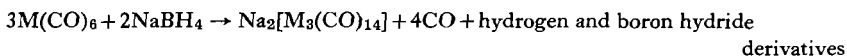


In general, the preparation of sodium derivatives of metal carbonyls by reduction with sodium metal either in ethereal solvents or in liquid ammonia produces mononuclear anions. In certain cases it is possible to prepare

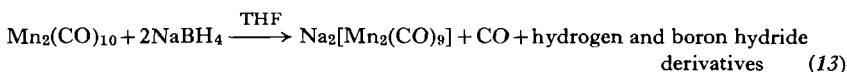
polynuclear anions by use of the milder reducing agent sodium borohydride, as illustrated by the following reactions



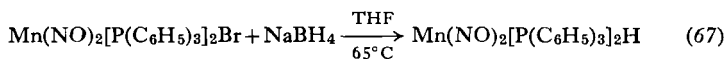
M = chromium (43, 65), molybdenum (43, 65), and tungsten (43)



M = chromium and molybdenum [boiling tetrahydrofuran (THF) solution] (66)



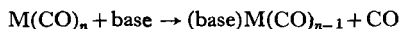
Sodium borohydride is also useful for the preparation of certain carbonyl and nitrosyl hydrides from the analogous halide derivatives,



M = iron (68) and ruthenium (53)

C. Metal Carbonyls and Anions

The preparation of metal carbonyl anions from Lewis bases and certain neutral metal carbonyl derivatives was described above. In general, such reactions involve disproportionation of the zero-valent metal atom in the metal carbonyl to a cation, with coordination of the base to the metal atom, and to the metal carbonyl anion. A different type of reaction between Lewis bases and metal carbonyls involves displacement of carbonyl groups in the metal carbonyl by the Lewis base without change in the oxidation state of the central metal atom, e.g.,

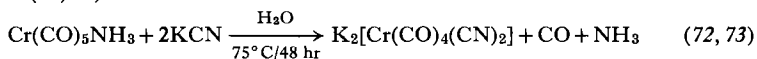


It is apparent that if the Lewis base is charged rather than neutral, the substituted metal carbonyl will have the same charge as the Lewis base. In this manner certain anionic metal carbonyls can be synthesized by the displacement of carbonyl groups with anionic Lewis bases. Frequently used for this type of reaction are the halide ions and cyanide ion. Many of these reactions have been carried out on the relatively stable hexacarbonyls of chromium, molybdenum, and tungsten, their derivatives or other related

hexacovalent compounds. The following equations illustrate this type of reaction.



M = Cr, Mo, and W, M' = *N*-methylpyridinium in dioxane solution (69); M = Cr, Mo, and W, M' = tetraethylammonium or tetrabutylammonium in diglyme solution (70, 71)



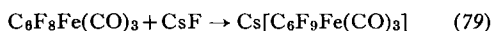
X = CN (liquid ammonia) (74); X = C \equiv CR (R = hydrogen, methyl or phenyl) (liquid ammonia) (75)



M = manganese (76); M = rhenium (methanol, 100° C, 4 hr) (77)

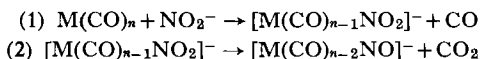


In addition to these reactions, where an anionic ligand displaces carbonyl groups or other neutral ligands such as ammonia, there is one example of the synthesis of an anionic metal carbonyl by *addition* of an anion (fluoride) to a neutral metal carbonyl:

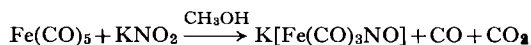


The uniqueness of this reaction is at least partially attributable to the unusual nature of the π -bonded fluorocarbon-iron carbonyl complex used as the starting material. Fluorocarbons such as octafluoro-1,3-cyclohexadiene containing more than one double bond are relatively rare.

In a related manner metal carbonyl derivatives may react with nitrite ion to form anionic nitrosyl derivatives, possibly according to the following reaction sequence



The only known example is the reaction between iron pentacarbonyl and potassium nitrite, preferably in the presence of a base producing the $[Fe(CO)_3NO]^-$ ion (8, 80, 81)

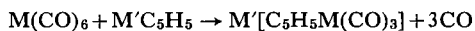


The $[HFe(CO)_4]^-$ ion can be used instead of iron pentacarbonyl in this reaction (8, 82).

Another frequently used reaction involves displacement of carbonyl groups in metal carbonyls with unsaturated hydrocarbons or their deriva-

tives to form π -bonded hydrocarbon complexes. If the unsaturated hydrocarbon which is used has a negative charge, an anionic metal carbonyl will result.

The only reported examples of this type of reaction are the reactions between the very stable cyclopentadienide anion and the hexacarbonyls of chromium, molybdenum, and tungsten



M = chromium, M' = potassium (dimethylformamide at 100-130°C) (83); M = molybdenum, M' = lithium (dioxane at 70-75°C) (83); M = tungsten, M' = lithium (dioxane at 110°C) (83); M = molybdenum or tungsten, M' = sodium (tetrahydrofuran at ~ 65°C) (52)

Nickel tetracarbonyl also forms an anionic derivative with sodium cyclopentadienide but it has not been characterized in detail. In this reaction polynuclear cyclopentadienylnickel anions may be formed (84).

III

FACTORS DETERMINING REACTIONS OF ALKALI METAL DERIVATIVES OF METAL CARBONYLS

One of the most important factors determining the stability of metal carbonyl derivatives and other transition metal complexes is the electronic configuration of the metal atom. Those complexes in which the transition metal has the configuration of the next inert gas are especially stable. Indeed at one time this was thought to be so important in metal carbonyl chemistry that all metal carbonyls were thought to have the inert gas configuration. The relatively recent discovery of vanadium hexacarbonyl (61, 85), in which the vanadium atom has one electron less than the inert gas configuration, demonstrated the existence of metal carbonyl derivatives without an inert gas configuration for the metal atom. However, vanadium hexacarbonyl is much less stable and much more reactive than chromium hexacarbonyl which has a similar structure but an inert gas configuration for the chromium atom.

Another carbonyl derivative in which at least one metal atom does not have the inert gas configuration is $(C_5H_5)_3Ni_3(CO)_2$ (86). In this case an analogous compound with inert gas configurations for all metal atoms is not known; however such a compound would contain different transition

metal atoms. Its preparation might therefore present certain synthetic problems.

In addition, several "metallocenes," [biscyclopentadienylmetal(II) derivatives] in which the metal atom does not have the inert gas configuration (those of vanadium, chromium, cobalt, and nickel are known). However, these compounds are much less stable and more reactive than the analogous ferrocene, in which the iron atom has the inert gas configuration.

Among metal complexes with formal oxidation states of $2+$ or higher not involving strongly double-bonding ligands, such as aquo- and ammine-complexes of chromium(III), cobalt(III), nickel(II), many compounds, some very stable, are known in which the metal atom does not have the inert gas configuration. Familiar examples are $[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}^{\text{II}}(2,2'\text{-bipyridyl})_3]^{2+}$, $\text{Fe}^{\text{III}}(\text{acetylacetonate})_3$, and $[\text{Ni}^{\text{II}}(\text{ethylenediamine})_3]^{2+}$. In the case of the neutral metal carbonyl and hydrocarbon-metal carbonyl derivatives in which the formal oxidation state of the metal atom is zero or $1+$, very few compounds without an inert gas configuration for the central metal atom are known. It thus appears that the lower the formal oxidation state on the metal atom, the greater the increase in stability of compounds with an inert gas configuration for the central metal atom relative to compounds without inert gas configuration for the central metal atom.

In most of the few metal carbonyl and cyclopentadienyl derivatives without an inert gas configuration for the central metal atom, such as $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_5\text{I}$ (87), $\text{C}_5\text{H}_5\text{VC}_7\text{H}_7$ (88), and $\text{C}_5\text{H}_5\text{CrC}_6\text{H}_6$ (89), the metal atom has exactly one electron less than the inert gas configuration. The only exceptions to this are the biscyclopentadienyl derivatives of vanadium, chromium, cobalt, and nickel in which the central metal atom has neither the inert gas configuration nor one electron less than this configuration.

No anionic metal carbonyl derivatives without an inert gas configuration for the central metal atom are known. A possible reason for this is the very low formal oxidation state of the metal atom.

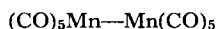
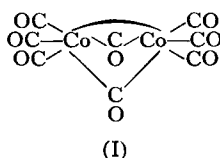
The stoichiometries of anionic metal carbonyls follow from the requirement of inert gas configuration for the metal atom. It is apparent, for example, why the usual carbonyl anions of vanadium, manganese, and cobalt have the formulas $[\text{V}(\text{CO})_6]^-$, $[\text{Mn}(\text{CO})_5]^-$, and $[\text{Co}(\text{CO})_4]^-$, respectively. In addition, in almost all neutral metal carbonyl derivatives, such as those prepared by reactions involving alkali metal derivatives of metal carbonyls, the metal atom will also have the inert gas configuration. A very few exceptions will arise; in these the metal atom will have one electron less than the inert gas

configuration. These compounds will be much less stable than the isostructural compounds with an inert gas configuration for the central metal atom.

If electronic configuration of the central metal atom were the sole factor determining the chemistry of alkali metal derivatives of the metal carbonyls, this chemistry would be relatively uninteresting. For example, manganese carbonyl chemistry would be identical to cobalt carbonyl chemistry, but each manganese compound would contain one more carbonyl group than the analogous cobalt compound. Vanadium carbonyl chemistry, likewise, would be identical to cobalt carbonyl chemistry, but each vanadium compound would contain two more carbonyl groups than the analogous cobalt compound. If this were the case, it would be possible to study the chemistry of one even-numbered transition metal (preferably iron since it is inexpensive) and one odd-numbered transition metal (such as manganese or cobalt) and then extrapolate with confidence to all other transition metals merely by addition or subtraction of an appropriate number of carbonyl groups.

However, consideration of the electronic configuration of metal atoms will not suffice to account for many of the features of the chemistry of the alkali metal derivatives of the metal carbonyls or any other branch of metal carbonyl or similar chemistry.

A good example is the comparison of the structures of the pure carbonyls of cobalt, manganese, and vanadium. The common carbonyl of cobalt, $\text{Co}_2(\text{CO})_8$ or $[\text{Co}(\text{CO})_4]_2$, is known to have a dimeric structure with a "bent" cobalt-cobalt bond, two bridging carbonyl groups, and six terminal carbonyl groups (I) (90). The only reported carbonyl of manganese,



(II)

$\text{Mn}_2(\text{CO})_{10}$ or $[\text{Mn}(\text{CO})_5]_2$, does not have a structure analogous to that of dicobalt octacarbonyl but with one more carbonyl group bonded to each metal atom. Instead, dimanganese decacarbonyl has two $\text{Mn}(\text{CO})_5$ groups linked together solely by a manganese-manganese bond (II) (91) with no bridging carbonyl groups.

The structure of vanadium carbonyl is again different from those of dimanganese decacarbonyl or dicobalt octacarbonyl. Despite an early report

to the contrary (92) vanadium hexacarbonyl is not dimeric but instead has a monomeric structure like that of chromium hexacarbonyl (85).

Such aspects of metal carbonyl structure may be explained by consideration of the coordination number of the central metal atom as an important factor in determining the stability of metal carbonyls. As is the case with other transition metal derivatives such as the ammines, octahedral hexacoordinate metal carbonyl derivatives seem to be especially favored. Thus, hexacoordinate chromium hexacarbonyl is obviously more stable and less reactive than pentacoordinate iron pentacarbonyl or tetracoordinate nickel tetracarbonyl. Moreover, hexacoordinate methylmanganese pentacarbonyl is indefinitely stable at room temperature (93) whereas pentacoordinate methylcobalt tetracarbonyl (55) rapidly decomposes at room temperature and heptacoordinate methylvanadium hexacarbonyl has never been reported, despite the availability of obvious starting materials for its preparation.

It is thus evident that in order to attain maximum stability in a metal carbonyl derivative, the central metal atom must be selected to give a *hexacoordinate derivative with an inert gas configuration for the central metal atom*. Penta- and tetracoordinated derivatives will be much less stable and hepta- and octacoordinated derivatives of the 3*d* transition metals (with exceptions to be discussed below) will very rarely, if at all, be capable of existence. Hepta- and octacoordinated derivatives of the 4*d* and 5*d* transition metals should be more stable than those of the 3*d* transition metals. However, very few are known, probably because most of them would involve elements such as zirconium and niobium, whose metal carbonyl chemistry is little known at present.

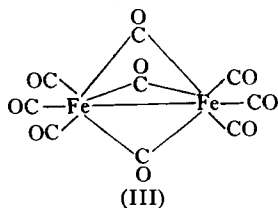
Some ligands frequently encountered in metal carbonyl chemistry appear to stabilize unusually high coordination numbers, apparently because they occupy significantly less space than the number of normal monodentate ligands contributing an equivalent number of electron pairs to the metal atom. These include the following types of ligands:

(1) *π -Bonded hydrocarbons, especially π -cyclopentadienyl*. Despite extensive debate (beyond the scope of this article) regarding the precise nature of the metal- π -cyclopentadienyl bond, it now appears that, whatever the detailed nature of the bonding, each π -cyclopentadienyl ring donates three electron pairs to the metal atom and thus occupies three coordination positions. However, because of its shape the cyclopentadienyl ring appears to be less

demanding sterically than three atoms, whether derived from monodentate ligands or from "arms" of chelating ligands, bonded separately to the metal atom. Although hexacoordinate π -cyclopentadienyl derivatives such as $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ appear to be the most stable compounds, heptacoordinate derivatives of the $3d$ transition metals, such as $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$, exhibit appreciable stability, and even octacoordinate derivatives of the $3d$ transition metals, such as $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ (94), are known. Similar effects are expected for other π -bonded hydrocarbon ligands, such as benzene and cycloheptatrienyl, but due to a lower stability of the metal–ligand bond, examples of derivatives of these ligands are much rarer.

(2) *Hydrogen*. Although hydrogen, like the halogens and alkyl groups, contributes one electron to the metal atom when forming a complex, it appears to be slightly less demanding sterically than the larger halogens and alkyl groups. Thus a heptacoordinate hydrogen derivative of the $3d$ transition metal, vanadium, of formula $\text{HV}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3]$ is known (11). Also, the unusual nine-coordinate $\text{K}_2[\text{ReH}_9]$ has been recently characterized (94a).

(3) *Compounds with one transition metal atom bonded to another transition metal atom*. A variety of compounds has been prepared in which one transition metal atom is bonded to another transition metal atom. In some cases the metal–metal bond does not appear to occupy a coordination position. For example, in $\text{Fe}_2(\text{CO})_9$ (III) each iron atom is bonded to seven other groups: three terminal carbonyl groups, three bridging carbonyl groups, and the other iron atom. The bonds from the six carbonyl groups occupy approximately the six positions of an octahedron with the iron–iron bond in the center of one of the faces (95).



In consideration of the relative stabilities of various coordination numbers it is of interest to compare the stabilities and reactivities of some of the more common metal carbonyl anions. Thus the hexacoordinate $[\text{V}(\text{CO})_6]^-$ ion, which is so stable that the diglyme adduct of the sodium salt can be handled in air (63), has not yet been observed to react with any alkyl halides to give

heptacoordinate compounds of the type $RV(CO)_6$ although, as will be seen below, numerous other reactions of this anion not involving increase of the coordination number have been described. However, the pentacoordinate $[Mn(CO)_5]^-$, which is very air-sensitive (5), has been observed to react with numerous alkyl halides to form stable hexacoordinate derivatives $RMn(CO)_5$. The tetracoordinate $[Co(CO)_4]^-$ reacts with alkyl halides to give pentacoordinate derivatives of the type $RCo(CO)_4$ but these compounds, probably because they have coordination number five, are much less stable than the $RMn(CO)_5$ derivatives. Thus $CH_3Co(CO)_4$ is an unstable liquid which decomposes even in the absence of air at $-35^\circ C$ (55), whereas $CH_3Mn(CO)_5$ is a white crystalline solid stable indefinitely at room temperature even in air (96).

Consideration of the stabilities of compounds of metals with various coordination numbers also accounts for the behavior of the reactive pentacoordinate $[Cr(CO)_5]^{2-}$. The very stable hexacoordinate $Cr(CO)_6$ can only be reduced to this anion by very powerful reducing agents such as the blue solutions of alkali or alkaline earth metals in liquid ammonia (41). The $[Cr(CO)_5]^{2-}$ anion is very reactive under conditions where hexacoordinate compounds of the type $Cr(CO)_5L$ may be formed (41, 72, 73, 97). However, the $[Cr(CO)_5]^{2-}$ anion has not yet been observed to react with two moles of halide to form heptacoordinate derivatives of the type $R_2Cr(CO)_5$.

It is also of interest to compare the acid dissociation constants for the carbonyl hydrides of vanadium, manganese, and cobalt. The heptavalent $HV(CO)_6$, which ionizes to form the hexavalent anion $[V(CO)_6]^-$ (11), and the pentavalent $HCo(CO)_4$, which ionizes to form the tetravalent anion $[Co(CO)_4]^-$ (98), are both strong acids, whereas the hexavalent $HMn(CO)_5$, which ionizes to form the pentavalent anion $[Mn(CO)_5]^-$ is a weak acid ($K = 0.8 \times 10^{-7}$) (5). These equilibria thus favor the hexacoordinate derivative when possible.

In a similar manner the data of Piper and Wilkinson (52) indicate that the reactivity of the pentacoordinate $[C_5H_5Fe(CO)_2]^-$ with alkyl and aryl halides to give hexacoordinate derivatives of the type $C_5H_5Fe(CO)_2R$ is greater than the reactivity of the hexacoordinate $[C_5H_5Mo(CO)_3]^-$ with the same alkyl and aryl halides to give the heptacoordinate derivatives of the type $C_5H_5Mo(CO)_3R$. For example, $Na[C_5H_5Fe(CO)_2]$ reacts with iodobenzene in tetrahydrofuran solution to give the phenyl derivative in 5% yield whereas $Na[Mo(CO)_3C_5H_5]$ fails to give a phenyl derivative under the same reaction conditions (52).

If the electronic configuration and coordination number of the central atom were the sole factors determining the reactions of anionic and other metal carbonyl derivatives, the chemistry of the anions $[M(CO)_5]^-$ ($M = Mn, Tc, Re$) and $[C_5H_5M(CO)_2]^-$ ($M = Fe, Ru, Os$), all with the same electronic configuration and coordination number, would be very similar to one another and, in addition, the carbonyl groups in these anions should be replaceable by other ligands analogous to the corresponding reactions involving the neutral molecules $M(CO)_5$ ($M = Fe, Ru, Os$) and $C_5H_5M(CO)_2$ ($M = Co, Rh, Ir$). However, there are many differences between the chemistry of these species, the following being illustrations:

(1) *Ease of substitution.* The carbonyl groups in iron pentacarbonyl may be substituted readily with numerous other ligands, such as unsaturated hydrocarbons, isocyanides, and certain phosphorus and sulfur derivatives. No analogous substitution reactions may be carried out with the $[Mn(CO)_5]^-$ anion. The substituted anion $[Mn(CO)_4P(C_6H_5)_3]^-$, although preparable by other methods (48, 49), cannot be obtained by the action of triphenylphosphine on salts of the $[Mn(CO)_5]^-$ anion.

(2) *Hydride stability.* The carbonyl hydrides $HMn(CO)_5$ (5) and $HRe(CO)_5$ (46, 47) are significantly more stable than $HTc(CO)_5$ (45) and $HFe(CO)_2C_5H_5$ (68).

(3) *Ease of decarbonylation of σ -allyl derivative.* The π -allyl derivative $C_3H_5Mn(CO)_4$ is obtained by heating the σ -allyl derivative $C_3H_5Mn(CO)_5$ (99, 100). However, heating the corresponding σ -allyl derivative $C_3H_5Fe(CO)_2C_5H_5$ fails to give the π -allyl derivative $C_3H_5FeCOC_5H_5$, ultraviolet irradiation being necessary (101).

(4) *Ease of decarbonylation of acyl derivatives.* Heating the acetyl derivative $CH_3COMn(CO)_5$ produces the methyl derivative $CH_3Mn(CO)_5$ (97, 102) but heating the corresponding acetyl derivative $CH_3COFe(CO)_2C_5H_5$ does not produce the corresponding methyl derivative, a complex decomposition occurring instead.

(5) *Reaction with 1,3-Dibromopropane.* 1,3-Dibromopropane reacts with the anions $[C_5H_5Fe(CO)_2]^-$ and $[Mn(CO)_5]^-$ to form the compounds $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ (103) and $(CH_2)_3[Mn(CO)_5]_2$ (104), respectively. Although the formulas of these two derivatives are analogous, the NMR spectra and other physical properties indicate them to be different types of compounds.

These differences in reactions may be attributed to differences in the strength of the metal-carbon monoxide bond in these metal carbonyl derivatives.

Carbon monoxide like other ligands, such as tertiary phosphines, olefins, isocyanides, amines, and water, bonds to a transition metal atom by donating an electron pair to the metal atom. However, in the metal carbonyls this bonding is supplemented to a very large extent by so-called "back-bonding" or "partial double-bonding" involving partial donation of one of the non-bonding d -electron pairs to the metal atom. This back-bonding is much stronger in metal derivatives of carbon monoxide than in metal derivatives of other ligands, even tertiary phosphines and isocyanides, and makes such a significant contribution to the total strength of the metal-carbon monoxide bond that carbon monoxide derivatives of the non-transition metals are unknown [with the possible exception of the very unstable boron hydride derivatives BH_3CO (105) and $\text{B}_4\text{H}_8\text{CO}$ (106)]. It thus appears that factors which influence the amount of back-bonding in the metal-carbon monoxide bond will have a large effect on the total strength of the bond. The following factors *increase* the strength of the metal-carbon monoxide bond by increasing the amount of back-donation of the nonbonding d electrons of the transition metal atom to the carbon monoxide:

- (1) *Negative charge on the metal atom.* This increased electron density naturally increases the tendency for the metal atom to donate electrons back to the carbon monoxide. The increased stability arising from this factor makes the carbon monoxide ligands in metal carbonyl anions inert to substitution by other ligands. Conversely, the carbon monoxide ligands in cationic metal carbonyls appear to be unusually labile and readily substituted. An excellent example is the recently discovered $[\text{Mn}(\text{CO})_6]^+$ cation (107). Despite the desirable coordination number of six and the inert gas configuration for the manganese atom, this cation is unstable, and is decomposed even by water.
- (2) *Substitution of carbon monoxide by other ligands.* It was noted above that metal atoms have a larger tendency to partially donate nonbonding d electrons to carbon monoxide than to any other ligand. Differently stated, carbon monoxide is a stronger acceptor than other ligands, such as tertiary phosphines or π -bonded aromatic rings. Substitution of carbon monoxide with other more weakly accepting ligands will therefore increase the amount of back-bonding of the metal atom to the remaining carbon monoxide

ligands. Consequently, the strength of the metal–carbon monoxide bond is greater in metal carbonyl derivatives in which some of the carbon monoxide ligands have been replaced by other ligands such as tertiary phosphines and π -cyclopentadienyl. This accounts for the difficulties in decarbonylating the cyclopentadienyliron dicarbonyl derivatives $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $(\sigma\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ as compared with the analogous manganese pentacarbonyl derivatives $\text{CH}_3\text{COMn}(\text{CO})_5$ and $(\sigma\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_5$, discussed above.

In addition to these two factors which influence the strength of the metal–carbon monoxide bond by clearly affecting the amount of “back-bonding” or partial double-bonding between the metal atom and the carbon monoxide ligand, there are two other factors which affect the strength of the metal–carbon monoxide bond.

(1) *Comparison between the 3d, 4d, and 5d transition metals.* It has been observed that molybdenum hexacarbonyl undergoes substitution reactions much more readily than the isoelectronic and isostructural hexacarbonyls of chromium and tungsten (108). It appears that the 4d transition metals form weaker bonds with carbon monoxide than the 3d or the 5d transition metals. In the case of compounds prepared from anionic metal carbonyls this effect should be especially noticeable in a comparison of the chemistry of derivatives of the anions $[\text{M}(\text{CO})_5]^-$ ($\text{M} = \text{Mn}, \text{Tc}, \text{Re}$). Unfortunately, the extreme rarity of the 4d transition metal of this group, technetium, has acted as a barrier to a detailed comparative investigation of the chemistry of these three anions. However, the lower stability of the technetium–carbon monoxide bond, compared with the analogous bonds of manganese and rhenium, appears to be manifested in the lower stability of $\text{HTc}(\text{CO})_5$ (45) as compared with $\text{HMn}(\text{CO})_5$ and $\text{HRe}(\text{CO})_5$, and in the isolation of a derivative [apparently $\text{Tc}_3(\text{CO})_{12}$] with only four carbonyl groups per technetium atom in attempts to prepare $\text{HTc}(\text{CO})_5$ (109).

(2) *Comparison between various coordination numbers.* The metal–carbon monoxide bonds in tetracoordinated and pentacoordinated metal carbonyls appear to be less stable than the metal–carbon monoxide bonds in the corresponding hexacoordinated metal carbonyls. For example, $[\text{Co}(\text{CO})_4]^-$ reacts with allyl halides at room temperature to produce directly the π -allyl derivative, $\text{C}_3\text{H}_5\text{Co}(\text{CO})_3$; the presumed pentacoordinate intermediate σ -allyl derivative $\text{C}_3\text{H}_5\text{Co}(\text{CO})_4$ is not isolable, losing carbon monoxide rapidly even at room temperature (110). In contrast to this behavior,

$[\text{Mn}(\text{CO})_5]^-$ reacts with allyl halides at room temperature to produce the hexacoordinate σ -allyl derivative $\text{C}_3\text{H}_5\text{Mn}(\text{CO})_5$ which must be heated to $\sim 60^\circ\text{C}$ before carbon monoxide is lost at an appreciable rate to form the π -allyl derivative $\text{C}_3\text{H}_5\text{Mn}(\text{CO})_4$ (99, 100). In addition, the pentacoordinate perfluoroacyl derivatives of cobalt, $\text{R}_f\text{COCO}(\text{CO})_4$ (38, 111, 112), lose carbon monoxide to form $\text{R}_f\text{Co}(\text{CO})_4$ at a lower temperature than the hexacoordinate perfluoroacyl derivatives of manganese, $\text{R}_f\text{COMn}(\text{CO})_5$ (38, 113), form the perfluoroalkyl derivatives, $\text{R}_f\text{Mn}(\text{CO})_5$. On the basis of present data, however, it is difficult to separate the effect of coordination number on the general stability of the molecule from the effect of coordination number on the stability of the metal-carbon monoxide bond.

In summary, metal carbonyl chemistry is largely determined by the following three factors:

- (1) *Electronic configuration of the central metal atom.* An inert gas configuration is favored, especially in compounds with an extremely low formal oxidation state of the central metal atom.
- (2) *Coordination number of the central metal atom.* Hexacoordinate derivatives are favored.
- (3) *Stability of the metal-carbon monoxide bond.* A low formal oxidation state, substitution of carbonyl groups by other ligands, and a hexacoordinate central metal atom of either the 3d or the 5d transition series favor a more stable metal-carbon monoxide bond.

In the following sections specific aspects of the chemistry of alkali metal and other anionic derivatives of metal carbonyls will be discussed. The role of the above three factors in influencing this chemistry will be demonstrated.

IV

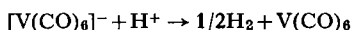
DERIVATIVES OF VANADIUM, NIOBIUM, AND TANTALUM

A. Vanadium Hexacarbonyl and Derivatives

The chemistry of carbonyl derivatives of vanadium [except $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$] is of very recent origin. Although the properties of vanadium hexacarbonyl were briefly described in 1959 (114), the first preparation of vanadium hexacarbonyl (from ditoluenovanadium and carbon monoxide) was des-

cribed in early 1960 (92). Several more convenient and efficient preparations of vanadium hexacarbonyl have subsequently appeared (61, 62, 63). Because of its recent discovery the chemistry of vanadium hexacarbonyl has probably not been investigated as thoroughly as that of the carbonyl derivatives of many other transition metals.

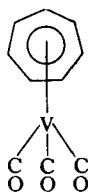
One of the characteristic features of vanadium carbonyl chemistry is the ease of formation of the very stable hexacoordinate $[\text{V}(\text{CO})_6]^-$ ion, which, unlike neutral $\text{V}(\text{CO})_6$, possesses the inert gas configuration. In two of the three methods for the preparation of vanadium hexacarbonyl from vanadium trichloride the anion $[\text{V}(\text{CO})_6]^-$ is initially formed (61, 62, 63). Upon acidification of the $[\text{V}(\text{CO})_6]^-$ anion hydrogen is liberated and vanadium hexacarbonyl produced



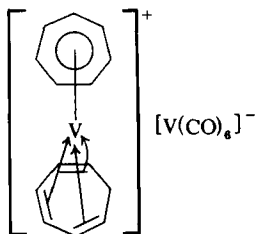
This reaction undoubtedly proceeds via the unstable heptacoordinate hydride $\text{HV}(\text{CO})_6$ (11). This hydride, like $\text{HCo}(\text{CO})_4$ and unlike $\text{HMn}(\text{CO})_5$, has been demonstrated to be a strong acid.

Conversion of the $[\text{V}(\text{CO})_6]^-$ anion to neutral $\text{V}(\text{CO})_6$ can be accomplished with hydrogen ion or with the selective oxidizing agent tropylium ion (115). Conversion of the neutral hexacarbonyl back to the anionic derivative can easily be accomplished either with reducing agents such as elemental sodium (64) or with numerous Lewis bases (see Section II, A). A more unusual method of obtaining the $[\text{V}(\text{CO})_6]^-$ anion from the neutral $\text{V}(\text{CO})_6$ is by treatment with cycloheptatriene.

The reaction between vanadium hexacarbonyl and cycloheptatriene was first utilized by Werner and Manastyrskyj to prepare π -cycloheptatrienyl-vanadium tricarbonyl (IV) (115), a dark green volatile solid soluble in nonpolar organic solvents. This compound is one of the relatively few π -cycloheptatrienyl derivatives. Werner and Manastyrskyj report the concurrent formation in this reaction of a brown solid insoluble in nonpolar



(IV)



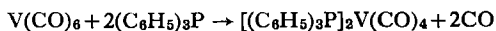
(V)

organic solvents but made no attempt to characterize this material. Later work by Calderazzo and Calvi (116) demonstrated that this brown rather unstable derivative was the $[\text{V}(\text{CO})_6]^-$ salt of the π -cycloheptatrienyl- π -cycloheptatriene-vanadium cation (V). This reaction between vanadium hexacarbonyl and cycloheptatriene is a unique example of a hydrocarbon without functional groups other than double bonds acting like a Lewis base in causing the disproportionation of a neutral metal carbonyl into an anionic metal carbonyl and a cationic derivative of the same metal and the hydrocarbon. The unusual stability of the $[\text{V}(\text{CO})_6]^-$ anion is perhaps at least partially the driving force for its formation in this reaction. Related investigations of reactions between vanadium hexacarbonyl and other hydrocarbon species might lead to similarly interesting results.

Salts of the $[\text{V}(\text{CO})_6]^-$ anion, especially those of large cations, are noteworthy in their resistance to air oxidation. Of particular significance is the diglyme-complexed sodium salt $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ formed by the reaction between vanadium trichloride, sodium, diglyme, and carbon monoxide under pressure. Unlike other mostly pyrophoric sodium derivatives of metal carbonyls, this yellow solid is sufficiently air stable to be handled and even stored for a few days without protection from air. It does appear to be light-sensitive, however, and storage in the dark is therefore recommended (117). This sodium derivative is much more stable than the sometimes pyrophoric (62) neutral vanadium hexacarbonyl and is thus a recommended form for storage of $\text{V}(\text{CO})_6$ species. Vanadium hexacarbonyl may be liberated from this sodium derivative as needed by treatment with phosphoric acid (63).

The stability of the $[\text{V}(\text{CO})_6]^-$ anion is also reflected in a diminished reactivity, especially towards reagents such as alkyl halides which would be expected to produce a generally unfavorable heptacoordinate derivative from the more greatly favored hexacoordinate anion. Reagents with oxidizing tendencies (such as nitrite ion, which might otherwise have been expected to form a nitrosyl derivative) oxidize the yellow solutions of $[\text{V}(\text{CO})_6]^-$ to greenish solutions, with gas evolution. The carbonyl derivative is completely destroyed (117).

Some triphenylphosphine-substituted anionic derivatives of vanadium carbonyl are known. Treatment of vanadium hexacarbonyl with triphenylphosphine in hexane solution gives the orange air-sensitive $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{V}(\text{CO})_4$ in 61.2% yield (39).



This derivative, like vanadium hexacarbonyl itself, has one electron less than the inert gas configuration and exhibits the expected paramagnetism. Upon reduction with sodium amalgam in ethanol or benzene it does *not* form the expected sodium salt $\text{Na}\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{V}(\text{CO})_4\}$. Instead a peculiar redistribution reaction occurs and the sodium salt $\text{Na}[(\text{C}_6\text{H}_5)_3\text{PV}(\text{CO})_5]$ is formed (39). Tetramethylammonium, tetraethylammonium, and tris(*o*-phenanthroline)nickel(II) salts of this anion may be obtained by metathesis (39). The hydride $\text{HV}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ (11) prepared by acidification of the sodium salt is a crystalline solid which is more stable but less acidic ($K = 1.5 \times 10^{-7}$) than the unsubstituted $\text{HV}(\text{CO})_6$. The greater stability and lower acidity of triphenylphosphine-substituted metal carbonyl hydrides as compared with the unsubstituted metal carbonyl hydride is a general phenomenon and other such systems will be encountered below.

B. Cyclopentadienylvanadium Carbonyl Derivatives

Cyclopentadienylvanadium tetracarbonyl may be reduced with sodium in liquid ammonia, the orange neutral derivative being converted to the yellow dinegative anion $[\text{C}_5\text{H}_5\text{V}(\text{CO})_3]^{2-}$ (40). Despite the desirable coordination number of six and inert gas configuration, derivatives of this anion are very air-sensitive, no doubt due to the low formal oxidation state of -1 for the vanadium atom. The carbonyl groups in this anion absorb at the unusually low infrared frequencies of 1748 and 1645 cm^{-1} , in the region more commonly associated with bridging carbonyl groups (118). This arises from a relatively low carbon–oxygen bond order in the carbonyl groups as a consequence of a relatively high vanadium–carbon bond order. This large degree of partial vanadium–carbon double-bonding arises from the large negative charge on the vanadium atom due to its low formal oxidation state.

The sodium derivative of the $[\text{C}_5\text{H}_5\text{V}(\text{CO})_3]^{2-}$ anion may be converted to salts of the heavier alkali metals, potassium, rubidium, and cesium, by metathesis with the appropriate iodides in liquid ammonia solution (40). Aqueous solutions are unstable except when very basic. Treatment of these solutions either with the $[(\text{C}_5\text{H}_5)_2\text{Co}]^+$ or the $[\text{Fe}(\text{o-phen})_3]^{2+}$ cations give precipitates which could not be characterized due to their tendency to decompose into $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ on drying or on attempted recrystallization. A deep green species, possibly a cyclopentadienylvanadium carbonyl derivative either not having the inert gas configuration or having more than one vanadium atom, may be extracted with pentane during acidification of

solutions of the $[\text{C}_5\text{H}_5\text{V}(\text{CO})_3]^{2-}$ anion. This green derivative was too unstable for characterization, rapid loss of $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ occurring during attempted isolation. It is, however, not the carbonyl hydride $\text{C}_5\text{H}_5\text{V}(\text{CO})_3\text{H}_2$, since it does not reform the $[\text{C}_5\text{H}_5\text{V}(\text{CO})_3]^{2-}$ anion on treatment with base.

C. Niobium and Tantalum Derivatives

Information on the carbonyl chemistry of niobium and tantalum is, to date, very meager. The main difficulty appears to be the reduction of the usual pentavalent derivatives of these metals to the very low formal oxidation states of metal carbonyl derivatives. Nevertheless, the yellow anions $[\text{M}(\text{CO})_6]^-$ ($\text{M} = \text{Nb}, \text{Ta}$) have been obtained by a method analogous to, but more difficult than, one of the preparations of the $[\text{V}(\text{CO})_6]^-$ anion. The method involves reduction of the pentachlorides with sodium metal in diglyme in the presence of high pressures of carbon monoxide (63). The niobium and tantalum derivatives are much more air-sensitive than the analogous vanadium derivative. The niobium derivative has not yet been obtained analytically pure (63). No chemistry of the $[\text{Nb}(\text{CO})_6]^-$ and the $[\text{Ta}(\text{CO})_6]^-$ ions has been reported, even conversion to the neutral carbonyl derivatives $[\text{M}(\text{CO})_6]_n$ ($\text{M} = \text{Nb}$ or Ta ; $n = 1$ or 2) or to the carbonyl hydride derivatives $\text{HM}(\text{CO})_6$ ($\text{M} = \text{Nb}, \text{Ta}$) still presenting unsolved problems.

These two anions and $\text{C}_5\text{H}_5\text{Nb}(\text{CO})_4$ (119) constituted the entire known carbonyl chemistry of niobium and tantalum, as of late 1963. However, in early 1964 details for a satisfactory preparation of $[\text{Na}(\text{diglyme})_2][\text{Nb}(\text{CO})_6]$ in the pure state were reported (119a). The anions $[\text{M}(\text{CO})_6]^-$ ($\text{M} = \text{V}, \text{Nb}$, and Ta) were found to react with cyclopentadienylmercuric chloride in tetrahydrofuran or 1,2-dimethoxyethane solution to give the cyclopentadienylmetal tetracarbonyls, $\text{C}_5\text{H}_5\text{M}(\text{CO})_4$, in greatly improved yields. This represents the first preparation of $\text{C}_5\text{H}_5\text{Ta}(\text{CO})_4$ (119a).

V

DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

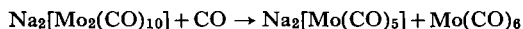
A. The Anions $[\text{M}(\text{CO})_5]^{2-}$ and $[\text{M}_2(\text{CO})_{10}]^{2-}$

In 1951 Rhomberg and Owen (120) reported the reaction of chromium hexacarbonyl with potassium hydroxide in alcoholic solution to give, after

acidification, a white, volatile, unstable crystalline substance which they suggested was the hydride $\text{H}_2\text{Cr}(\text{CO})_5$. This reaction has never been confirmed, and later investigations (3, 4) suggest other possibilities for the product of Rhomberg and Owen.

The first well-authenticated preparation of the $[\text{Cr}(\text{CO})_5]^{2-}$ anion was carried out by Behrens and Weber (41) and involved the reduction of chromium hexacarbonyl with elemental sodium, lithium, calcium, or barium in liquid ammonia solution. It is not surprising that such a powerful reducing agent is necessary to effect the reduction of the very stable hexacoordinate chromium hexacarbonyl to the less stable pentacoordinate $[\text{Cr}(\text{CO})_5]^{2-}$ anion. In a subsequent report by Podall and associates the reduction of chromium hexacarbonyl with sodium amalgam in tetrahydrofuran or diglyme solution (42) is described. The same report also describes the direct preparation of the $[\text{Cr}(\text{CO})_5]^{2-}$ anion from chromium trichloride by treatment with elemental sodium in diglyme solution under carbon monoxide pressure.

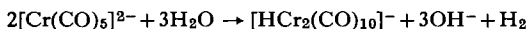
The reduction of molybdenum and tungsten hexacarbonyls by sodium in liquid ammonia to form the $[\text{M}(\text{CO})_5]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) anions is less satisfactory, because of the tendency for side reactions to occur in these systems leading to an impure product. An alternative route to the molybdenum derivative (65) involves first the reduction of molybdenum hexacarbonyl with sodium borohydride in liquid ammonia at $\sim +40^\circ \text{C}$ to produce the $[\text{Mo}_2(\text{CO})_{10}]^{2-}$ anion. This $[\text{Mo}_2(\text{CO})_{10}]^{2-}$ anion may then be treated with carbon monoxide under pressure at $\sim 150^\circ \text{C}$ to form an equimolar mixture of $[\text{Mo}(\text{CO})_5]^{2-}$ and molybdenum hexacarbonyl, the latter being readily separated by sublimation



One of the less desirable features of this preparation of $\text{Na}_2[\text{Mo}(\text{CO})_5]$ is the necessity for working with liquid ammonia so far above its boiling point. This creates a high pressure in the system, leading to frequent rupture of the sealed glass tubes in which the reaction is carried out. This synthesis may also be applied to the analogous chromium derivatives (65) but appears to offer no advantage over the more direct reduction of chromium hexacarbonyl with sodium in liquid ammonia described above. The anion $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ may be reduced with sodium in liquid ammonia to form the $[\text{Cr}(\text{CO})_5]^{2-}$ anion. This cleavage of the chromium–chromium bond in $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ with sodium to give the mononuclear anion is entirely

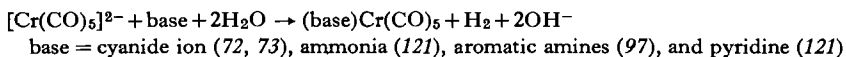
analogous to the now well-known cleavage of the manganese-manganese bond in $\text{Mn}_2(\text{CO})_{10}$ to give $[\text{Mn}(\text{CO})_5]^-$.

The sodium salts $\text{Na}_2[\text{Cr}(\text{CO})_5]$ and $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ are yellow solids. Due to the low formal oxidation state of the chromium atom, they are extremely sensitive to air oxidation and must be handled in an inert atmosphere with rigorous exclusion of air. As might be expected from its coordination number of five, the mononuclear $[\text{Cr}(\text{CO})_5]^{2-}$ anion is decomposed by water



This decomposition is inhibited in strongly basic solution.

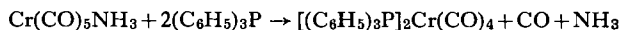
Despite this sensitivity to water many reactions of $[\text{Cr}(\text{CO})_5]^{2-}$ with other reagents, especially bases, may be carried out in aqueous solution. In the case of bases the reaction occurs according to the following scheme



In these reactions the water serves an essential although unusual function, oxidizing the chromium (−II) atom in the $[\text{Cr}(\text{CO})_5]^{2-}$ anion to chromium(O) in the $(\text{base})\text{Cr}(\text{CO})_5$ derivatives. No doubt an important driving force in this reaction is the conversion of the pentacoordinate $[\text{Cr}(\text{CO})_5]^{2-}$ to the more stable hexacoordinate $(\text{base})\text{Cr}(\text{CO})_5$. The aromatic amines which have been used in this reaction include aniline and *o*-phenylenediamine, which give derivatives with one $\text{Cr}(\text{CO})_5$ group; *m*- and *p*-phenylenediamines, which give derivatives with two $\text{Cr}(\text{CO})_5$ groups; and even 1,3,5-triaminobenzene, which gives a derivative with three $\text{Cr}(\text{CO})_5$ groups (97). It is of interest that the aliphatic amine 1,2-cyclohexanediamine gives the chelate derivative $(1,2\text{-cyclohexanediamine})\text{Cr}(\text{CO})_4$, probably due to its higher basicity. Ammonia, besides forming $\text{Cr}(\text{CO})_5\text{NH}_3$, forms smaller quantities of $\text{Cr}(\text{CO})_4(\text{NH}_3)_2$ and $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$ in its reaction with aqueous $[\text{Cr}(\text{CO})_5]^{2-}$ (121).

In general the $(\text{amine})\text{Cr}(\text{CO})_5$ compounds are yellow solids of variable air-sensitivity. The compounds derived from the aromatic amines are somewhat air-sensitive (97), whereas the pyridine and ammonia derivatives are air-stable (121). The pyridine and ammonia derivatives may be sublimed at 55° and 70° C, respectively, in a high vacuum, the higher sublimation temperature of the lower molecular weight ammonia derivative probably arising from hydrogen bonding. They may undergo substitution reactions

with other bases. Thus $\text{Cr}(\text{CO})_5\text{NH}_3$ reacts with triphenylphosphine as follows



A feature absent from the chemistry of the $[\text{Cr}(\text{CO})_5]^{2-}$ ion is the reaction with organic halides to form $\text{R}_2\text{Cr}(\text{CO})_5$ derivatives. No doubt such derivatives would be very unstable due to the heptacoordinate chromium atom. In an attempt to make the hydride $\text{H}_2\text{Cr}(\text{CO})_5$ an aqueous solution of $[\text{Cr}(\text{CO})_5]^{2-}$ was acidified in the presence of diethyl ether (121). The ether became yellow, but no $\text{H}_2\text{Cr}(\text{CO})_5$ or other species of interest could be isolated from this unstable solution.

B. The Anions $[\text{M}(\text{CO})_5\text{X}]^-$ and $[\text{M}(\text{CO})_4\text{X}_2]^{2-}$

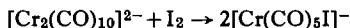
The hexacarbonyls of chromium, molybdenum, and tungsten react with a variety of Lewis bases to form very stable also hexacoordinate substitution products. If the Lewis base is anionic a metal carbonyl anion will result as discussed above.

For example, if one of the hexacarbonyls is heated with an ionic halide in an ethereal solvent, salts of the $[\text{M}(\text{CO})_5\text{X}]^-$ anions are formed (69, 70, 71). Useful in these reactions are *N*-methylpyridinium halides, because of their relatively high solubility in organic solvents. Tetraalkylammonium salts may also be used, but with somewhat less satisfactory results (70, 71). Even the alkali metal halides form $[\text{M}(\text{CO})_5\text{X}]^-$ ions when heated with the metal hexacarbonyls under appropriate conditions (70, 71). The yields are much poorer, however, due to the lower solubility of the alkali metal halides in organic solvents. In addition the products with alkali metal cations appear to be much less stable than those with the quaternary ammonium cations (70, 71). The halide ions may be chloride, bromide, and iodide, especially the latter. Diglyme (70, 71), dioxane (69), and tetrahydrofuran (122) have been used as solvents. The lowest boiling of these, tetrahydrofuran (b.p. 65°C), is probably only appropriate for reactions involving the especially reactive molybdenum hexacarbonyl, but this has not been definitively demonstrated for this particular reaction.

Wilkinson and Moore were the first to describe a reaction between a metal hexacarbonyl and an ionic halide derivative. In their work molybdenum hexacarbonyl and *N*-methylpyridinium iodide were heated in tetrahydrofuran solution (122). They erroneously formulated the product as

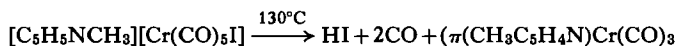
the iodide of the π -*N*-methylpyridiniummolybdenum tricarbonyl cation rather than as the *N*-methylpyridinium salt of the $[\text{Mo}(\text{CO})_5\text{I}]^-$ anion. This misconception was corrected by Fischer and Öfele (69), who also prepared the chromium and tungsten analogs. Later Abel and co-workers (70, 71) prepared other salts of these anions.

An alternative but much less convenient preparation of the $[\text{Cr}(\text{CO})_5\text{I}]^-$ anion involves cleavage of the chromium–chromium bond of $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ with iodine (87)

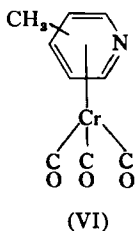


This reaction is analogous to the cleavage of the manganese–manganese bond in $\text{Mn}_2(\text{CO})_{10}$ with iodine to give $\text{Mn}(\text{CO})_5\text{I}$ (123).

These salts of the $[\text{M}(\text{CO})_5\text{I}]^-$ anions ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$) are yellow to orange solids which may be handled in air for brief periods. On heating in vacuum the *N*-methylpyridinium salt of the $[\text{Cr}(\text{CO})_5\text{I}]^-$ anion is converted in very low yield to the π -complex- π C-methylpyridine-chromium tricarbonyl (VI) (69), a red volatile crystalline solid



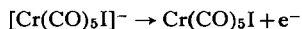
The position of substitution of the methyl group on the pyridine ring has not yet been demonstrated, possibly owing to the very small quantities of



material available. This derivative is the only known compound with a pyridine ring system π -bonded to a transition metal. All other reported attempts to prepare such systems (69) have instead resulted in derivatives where the nitrogen atom of the pyridine ring donates an electron pair to the transition metal, the carbon atoms of the pyridine ring not participating in the bonding.

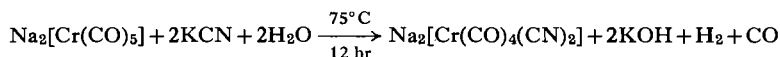
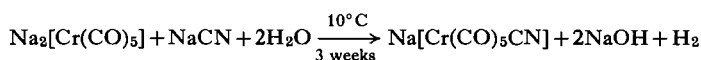
Another characteristic reaction of the $[\text{Cr}(\text{CO})_5\text{I}]^-$ anion is its oxidation in weakly acidic aqueous solution with triiodide ion, iron(III), or hydrogen peroxide to give the neutral $\text{Cr}(\text{CO})_5\text{I}$, a deep blue, thermally unstable,

volatile (sublimes at $\sim 30^\circ\text{C}$ in high vacuum) solid, insoluble in water but soluble in organic solvents to give deep blue solutions (87)

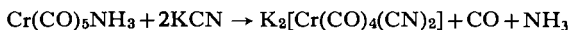


$\text{Cr}(\text{CO})_5\text{I}$ is isoelectronic with $\text{V}(\text{CO})_6$ and like the latter exhibits the expected paramagnetism for a species containing one unpaired electron. Chromium pentacarbonyl iodide appears to be more stable to oxidation but less stable to thermal decomposition than vanadium hexacarbonyl. This higher oxidative stability of $\text{Cr}(\text{CO})_5\text{I}$ as compared with that of $\text{V}(\text{CO})_6$ may be due to the higher formal oxidation state of the central metal atom of $\text{Cr}(\text{CO})_5\text{I}$.

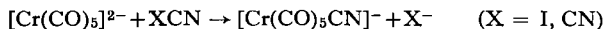
Cyanide-substituted chromium carbonyl anions have also been prepared. Treatment of $\text{Na}_2[\text{Cr}(\text{CO})_5]$ with aqueous sodium or potassium cyanides may lead either to bright yellow $\text{Na}[\text{Cr}(\text{CO})_5\text{CN}]$ or colorless $\text{Na}_2[\text{Cr}(\text{CO})_4(\text{CN})_2]$ depending on the reaction conditions (73):



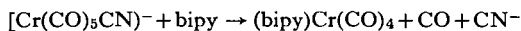
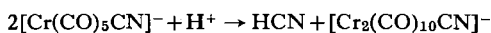
The $[\text{Cr}(\text{CO})_4(\text{CN})_2]^{2-}$ anion may also be obtained as the potassium salt by treatment of $\text{Cr}(\text{CO})_5\text{NH}_3$ with aqueous potassium cyanide at 75°C for 48 hours (73); displacement of one mole each of ammonia and carbon monoxide occurring



An alternative method of preparation of the $[\text{Cr}(\text{CO})_5\text{CN}]^-$ anion involves oxidation of the $[\text{Cr}(\text{CO})_5]^{2-}$ anion with cyanogen or iodine monocyanide (72, 87)



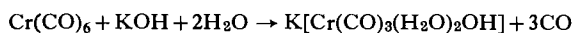
The alkali metal salts of these anions may be converted to the $[\text{Ni}(o\text{-phen})_3]^{2+}$ salts by metathesis (73). The $[\text{Cr}(\text{CO})_5\text{CN}]^-$ anion may be converted to the dimeric $[\text{Cr}_2(\text{CO})_{10}\text{CN}]^-$ anion on treatment with acid (72) and to $(\text{bipy})\text{Cr}(\text{CO})_4$ on heating with 2,2'-bipyridyl in aqueous ethanol at 80°C for 48 hours.



C. Miscellaneous Chromium, Molybdenum, and Tungsten Carbonyl Anions Other Than Cyclopentadienyl Derivatives

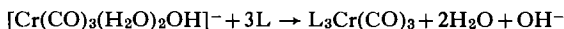
Treatment of the hexacarbonyls of chromium, molybdenum, and tungsten with aqueous or alcoholic hydroxide ion at elevated temperatures leads to a rather bewildering variety of anionic derivatives with hydroxide, water, and even alcohol substituents. Most of these derivatives have been characterized mainly by analysis.

Chromium hexacarbonyl was originally reported to react with aqueous ethanolic or methanolic potassium hydroxide in a sealed tube at $\sim 100^\circ\text{C}$ to produce the yellow $[\text{Cr}(\text{CO})_3(\text{H}_2\text{O})_2\text{OH}]^-$ anion (3)

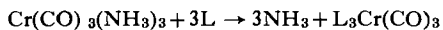


This anion may be considered as being derived from triaquochromium tricarbonyl, $\text{Cr}(\text{CO})_3(\text{H}_2\text{O})_3$, by loss of a proton. Attempts to prepare $\text{Cr}(\text{CO})_3(\text{H}_2\text{O})_3$ by treatment of this anion with water or acids have failed, apparently due to interfering side reactions and decomposition (3).

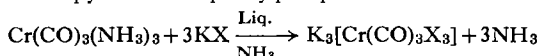
This chromium carbonyl anion is a useful precursor to chromium tricarbonyl derivatives of the types $\text{Cr}(\text{CO})_3\text{L}_3$ (L = ammonia or isocyanides) and $[\text{Cr}(\text{CO})_3\text{X}_3]^{3-}$ (74).



The methyl and *p*-anisyl isocyanide derivatives are white and yellow solids, respectively (74). The ammonia derivative $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$ forms yellow needles, which unlike $\text{Cr}(\text{CO})_6$ are air-sensitive. This air-sensitivity of $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$ may arise from the negative charge on the chromium atom, resulting from the inability of the three electron pairs of the three NH_3 ligands to remove electron density by partial double bonding with the transition metal atom. Because of the lack of metal-nitrogen double-bonding, the weakly bonded ammonia ligands are lost in a vacuum, and are replaceable by other ligands such as pyridine, triphenylphosphine, acetylides, or cyanide (74, 75)



L = pyridine or triphenylphosphine



L = cyanide, acetylides, methylacetylides, or phenylacetylides

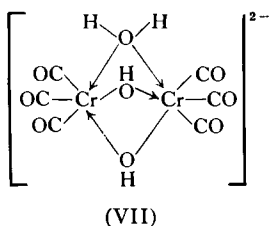
The triphenylphosphine derivative has not been obtained pure by this method. Later, however, compounds of the type $[(\text{C}_6\text{H}_5\text{P})_3]\text{M}(\text{CO})_3$

(M = Cr, Mo) were obtained pure by the reaction between triphenylphosphine and the appropriate cycloheptatriene-metal tricarbonyl (124). The pyridine derivative prepared at 90° C is a red solid (74). The reaction of $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$ with *o*-phenanthroline at 40–50° C was found to yield the tetracarbonyl derivative (*o*-phen) $\text{Cr}(\text{CO})_4$ in a complex reaction rather than a tricarbonyl derivative, undoubtedly because of the tendency for *o*-phenanthroline to act as a bidentate chelating ligand (74). The anion $[\text{Cr}(\text{CO})_3(\text{CN})_3]^{3-}$ was isolated as the diammoniate of the potassium salt, an unstable light yellow solid (74). The corresponding acetylide derivatives $\text{K}_3[\text{Cr}(\text{CO})_3(\text{C}\equiv\text{CR})_3]$ are moisture- and air-sensitive solids ranging in color from olive-green for the hydrogen derivative to orange for the phenyl derivative (75).

In a later study (4) the product obtained from chromium hexacarbonyl and ethanolic base was found to be the anion $[(\text{CO})_3\text{Cr}(\text{OH})_3\text{Cr}(\text{CO})_3\text{H}]^{2-}$ formed according to the following equation (4)



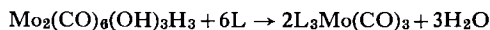
A possible structure for this anion (VII) contains two bridging hydroxide ions and one bridging water molecule. This study casts doubt upon the existence of the $[\text{Cr}(\text{CO})_3(\text{H}_2\text{O})_2\text{OH}]^-$ anion (3) discussed above.



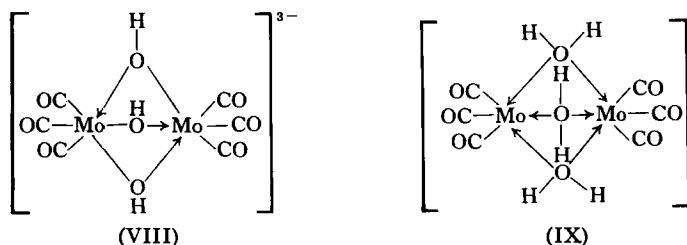
The analogous base reaction with molybdenum hexacarbonyl yields the anion $[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]^{3-}$ (4)



Acidification of this anion with hydrochloric acid yields the free acid $\text{Mo}_2(\text{CO})_6(\text{OH})_3\text{H}_3$ as bright yellow crystals. On treatment of $\text{Mo}_2(\text{CO})_6(\text{OH})_3\text{H}_3$ with various ligands such as triphenylphosphine, triphenylarsine, dimethylsulfoxide, or triphenylphosphine oxide at room temperature, compounds of the type $\text{L}_3\text{Mo}(\text{CO})_3$ are formed (4)



This method of preparation of $L_3Mo(CO)_3$ compounds is not as convenient, however, as the more recently discovered reaction of these ligands with cycloheptatriene-molybdenum tricarbonyl (124). Possible structures for the derivatives $[Mo_2(CO)_6(OH)_3]^{3-}$ and $Mo_2(CO)_6(OH)_3H_3$ are (VIII) and (IX), respectively.



The reaction between hydroxide ion and tungsten hexacarbonyl is even more complex. At 80–100° C the anions $[W_2(CO)_6(OH)_2(CH_3OH)_3]^{2-}$ and $[W_2(CO)_6(OH)_2(CH_3OH)_2]^{4-}$ are formed in methanol solution, whereas at 130° C the trinuclear anion $[W_3(CO)_9(OH)(OCH_3)(CH_3OH)]^{3-}$ is formed (125). Treatment of $[W_2(CO)_6(OH)_2CH_3OH]^{4-}$ with hydrochloric acid yields the derivatives $W_3(CO)_9(OH)_2(H_2O)H_4$ and $W_2(CO)_6(OH)_3H_3$ (126). Treatment of $W_3(CO)_9(OH)_2(H_2O)H_4$ with certain ligands at 70–90° C produces the mononuclear derivatives $L_3W(CO)_3$ (126). The structures of these derivatives are not yet understood.

Another type of polynuclear anion may be obtained by refluxing chromium or molybdenum hexacarbonyl with sodium borohydride in tetrahydrofuran to give the sodium salts of the black trinuclear $[M_3(CO)_{14}]^{2-}$ ($M = Cr, Mo$) anions (66). These species have not yet been investigated in detail.

D. The Anions $[C_5H_5M(CO)_3]^-$

The anions $[C_5H_5M(CO)_3]^-$ ($M = Cr, Mo, W$) and the corresponding derivatives of substituted cyclopentadienes may be prepared by the following three methods:

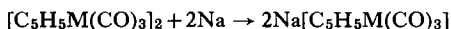
(1) *Heating the metal hexacarbonyl with an alkali metal cyclopentadienide in an ethereal solvent:*



This reaction may be regarded as the displacement of three carbonyl groups of the metal hexacarbonyl with the aromatic cyclopentadienide ion in a

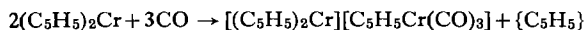
manner completely analogous to the reactions between the metal hexacarbonyls and benzene or its substitution products (127). Suitable reaction systems include potassium cyclopentadienide with chromium hexacarbonyl at 100–130° C in dimethylformamide (83), sodium cyclopentadienide with chromium hexacarbonyl in boiling diglyme (117), lithium cyclopentadienide with molybdenum hexacarbonyl in dioxane at 70–75° C (83), sodium cyclopentadienide with molybdenum hexacarbonyl in boiling tetrahydrofuran (52), lithium cyclopentadienide with tungsten hexacarbonyl in dimethylformamide at 110° C (83), and sodium cyclopentadienide with tungsten hexacarbonyl in boiling tetrahydrofuran (52) or 1,2-dimethoxyethane (117). The ease of displacement of carbonyl groups with cyclopentadienide anion appears to increase in the series $\text{Cr}(\text{CO})_6 < \text{W}(\text{CO})_6 < \text{Mo}(\text{CO})_6$ (52).

(2) *Reduction of the dimeric $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]_2$ with sodium (44) or sodium amalgam (128) in a tetrahydrofuran solution:*



This method has the disadvantage that prior preparation of the cyclopentadienylmetal tricarbonyl dimers is necessary, either from the metal hexacarbonyl and cyclopentadiene or its dimer (128, 129) or in the cases of certain substituted derivatives from the metal hexacarbonyl and fulvene derivatives (44). Neither of these preparative methods works in the case of the chromium derivative $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$, which must be obtained either from the anion $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]^-$ or from $(\text{C}_5\text{H}_5)_2\text{Cr}$ (see below). This method has the advantage, however, that the solution of the sodium derivative $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ is free from sodium cyclopentadienide, a possible complicating impurity in certain reactions.

(3) *Reaction of $(\text{C}_5\text{H}_5)_2\text{Cr}$ with carbon monoxide.* This specific method for chromium, carried out under pressure at 100–110° C, gives the brown-black $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]^-$ salt of the rarely encountered $[(\text{C}_5\text{H}_5)_2\text{Cr}]^+$ cation (130)



The alkali metal salts of the anions $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are yellow solids which, like the salts of the also hexacoordinate $[\text{V}(\text{CO})_6]^-$ anion, may be handled for short periods in air. However, the use of an inert atmosphere for handling these cyclopentadienyl derivatives is preferable. This behavior contrasts with that of the penta- and tetracoordinate anions such as $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$, $[\text{Mn}(\text{CO})_5]^-$, and $[\text{Co}(\text{CO})_4]^-$, which are instantly

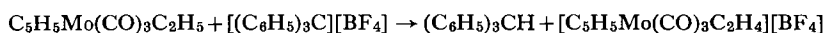
oxidized by air and for which the use of an inert atmosphere for handling is mandatory.

Despite the coordination number of six for the central metal atom in the anions $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), reaction with certain alkyl halides to form the heptacoordinate derivatives $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{R}$ occurs, at least in the cases of the molybdenum and tungsten derivatives. The properties of these derivatives are described in Table II. In some cases the yields in these reactions are very good. For example, $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ reacts with methyl iodide to produce the methyl derivative $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$ in 90% yield (52). Analogous reactions of $\text{Na}[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]$ with alkyl halides such as CH_3I are only vaguely mentioned in the literature (53). No analytical data or physical properties have been reported for the chromium compounds.

The alkyl compounds $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{R}$ ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{methyl, ethyl, or isopropyl}$) are yellow solids which may be handled for at least brief periods in the air and which may be purified easily by vacuum sublimation (52). The tungsten compounds appear to be somewhat more stable than those of molybdenum. The methyl derivative $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$ is stable almost indefinitely in the air. In the preparation of these compounds methyl and ethyl iodides were found to be more reactive than the secondary halide 2-iodopropane, which in turn was found to be more reactive than iodobenzene, the latter giving no product at all when treated with $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ under conditions suitable for reaction with the other halides (52).

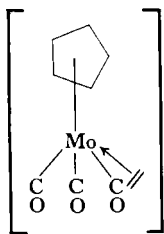
An early attempt to prepare the acyl derivatives from acyl halides and $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ was unsuccessful (102). However, more recently the perfluoroacyl derivatives, $\text{C}_3\text{F}_7\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ (113) and $\text{CF}_3\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ (117), and their tungsten analogs (117) have been obtained from $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ ($\text{M} = \text{Mo}$ or W) and heptafluorobutyryl chloride and trifluoroacetic anhydride, respectively.

A few interesting reactions of the alkyl derivatives $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{R}$ have been observed. Abstraction of hydride ion from $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$ with triphenylmethyl tetrafluoroborate gives the tetrafluoroborate of the π -cyclopentadienyl- π -ethylenemolybdenum tricarbonyl cation, $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_4][\text{BF}_4]$ (X), as golden crystals (131, 132)

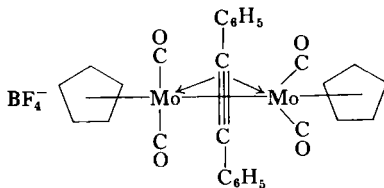


Treatment of the methyl derivative $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$ with diphenylacetylene gives tetraphenylcyclopentadiene and diphenylacetylenebis-(cyclopentadienylmolybdenum dicarbonyl) (XI) (133). (XI) may also be

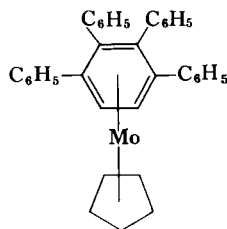
obtained from the reaction between cyclopentadienylmolybdenum tricarbonyl hydride or cyclopentadienylmolybdenum tricarbonyl dimer and diphenylacetylene. Reaction between the ethyl derivative $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$ and diphenylacetylene gives methyltetraphenylcyclopentadiene and a low yield of brown crystals, m.p. 207°C , believed from the infrared spectrum and analysis to be 1,2,3,4-tetraphenylbenzenecyclopentadienylmolybdenum (XII) (133). In this reaction the two carbons of the ethyl group are incorporated into the π -complexed substituted benzene ring. It must be pointed out, however, that the magnetic properties and molecular weight of (XII) have not yet been reported.



(X)

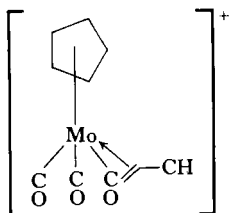


(XI)

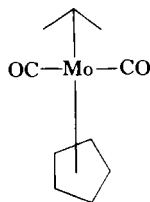


(XII)

The reaction between allyl chloride and $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ in tetrahydrofuran has been found to give the σ -allyl derivative $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{—CH}_2\text{—CH=CH}_2$ as a yellow liquid, m.p. $\sim -5^\circ\text{C}$, which may be purified by distillation at $40^\circ\text{C}/0.001\text{ mm}$ (131). Treatment of this compound with hydrogen halide gives the yellow π -cyclopentadienyl- π -propene-molybdenum tricarbonyl cation $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_3\text{H}_6]^+$ (XIII), which may be isolated as the hexafluorophosphate or the hexachloroplatinate. Heating the σ -allyl derivative gives only trace quantities of the corresponding π -allyl



(XIII)



(XIV)

derivative, the major product of this decomposition being $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$. However, by ultraviolet irradiation of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_2\text{—CH=CH}_2$ the

TABLE II
SOME ALKYL AND ACYL METAL CARBONYL DERIVATIVES

Compounds	Color	M.p. (°C)	B.p. or sublimation temp. (°C/mm)	Reference
(A) $\text{RM}(\text{CO})_3\text{C}_5\text{H}_5$ (M = Cr, Mo, W) Derivatives				
$\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	124° (dec.)	subl. 25–50°/0.001	52
$\text{C}_2\text{H}_5\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	77.5–78.5° (dec.)	subl. 25–50°/0.001	52
$(\text{CH}_3)_2\text{CHMo}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	29–30°	subl. 25–50°/0.001	52
$\text{CH}_2=\text{CHCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	~ –5°	40°/0.001	131
$\text{HCF}_2\text{CF}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	53–54°	subl. 25°/0.1	137
$\text{CF}_3\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	64–65°	subl. ~ 70°/0.1	117
$\text{C}_3\text{F}_7\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow-orange	46–47°	subl. ~ 70°/0.1	113, 117
$\text{CH}_3\text{W}(\text{CO})_3\text{C}_5\text{H}_5$	Lemon yellow	145°	subl. ~ 25–50°/0.001	52
$\text{C}_2\text{H}_5\text{W}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	93°	subl. ~ 25–50°/0.001	52
$\text{HCF}_2\text{CF}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	65°	—	137
$\text{CF}_3\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow	79.5–81.5°	subl. ~ 70°/0.1	117
$\text{C}_3\text{F}_7\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$	Yellow-orange	53–55°	subl. ~ 70°/0.1	117
(B) $\text{RM}(\text{CO})_5$ (M = Mn, Re) Derivatives				
$\text{CH}_3\text{Mn}(\text{CO})_5$	White	95°	20°/2	93, 96
$\text{CH}_3\text{Re}(\text{CO})_5$	White	120°	42.5°/1.5	151
$\text{C}_6\text{H}_5\text{CH}_2\text{Mn}(\text{CO})_5$	Pale yellow	37.5°	Volatile	96
$\text{C}_6\text{H}_5\text{CH}_2\text{Re}(\text{CO})_5$	Bright yellow	33–34°	60°/"high vacuum"	151
$\text{C}_2\text{H}_5\text{Mn}(\text{CO})_5$	—	Liquid	—	151
$\text{C}_2\text{H}_5\text{Re}(\text{CO})_5$	—	Liquid	—	53
$\text{CH}_2=\text{CHCH}_2\text{Mn}(\text{CO})_5$	Yellow	Liquid	~ 25°/0.001	99, 100

$\text{CF}_3\text{CF}=\text{CFMn}(\text{CO})_5$	White	76°	60°/3	38, 113
$\text{C}_3\text{N}_3\text{Cl}[\text{Mn}(\text{CO})_5]_2$	White	~ 170° (dec.)	100°/0.1	104
$\text{CH}_3\text{COMn}(\text{CO})_5$	White	54–55°	Volatile	96
$\text{CH}_3\text{CRe}(\text{CO})_5$	Pale yellow	80–81°	Volatile	151
$\text{C}_6\text{H}_5\text{COMn}(\text{CO})_5$	White	95–96°	Volatile	96
$\text{C}_6\text{H}_5\text{Mn}(\text{CO})_5$	White	52°	Volatile	96
$\text{C}_6\text{H}_5\text{CRe}(\text{CO})_5$	Canary yellow	120° (dec.)	80–100°/"high vacuum"	151
$\text{C}_6\text{H}_5\text{Re}(\text{CO})_5$	White	46–47°	40°/"high vacuum"	151
$\text{C}_2\text{H}_5\text{COMn}(\text{CO})_5$	White	58°	49°/3.5	151
$p\text{-CH}_3\text{C}_6\text{H}_4\text{COMn}(\text{CO})_5$	Lemon yellow	98°	Volatile	149
$p\text{-CH}_3\text{C}_6\text{H}_4\text{Mn}(\text{CO})_5$	—	43°	Volatile	149
$\text{CF}_3\text{COMn}(\text{CO})_5$	Pale yellow	55–56°	55°/15	38, 102, 149
$\text{CF}_3\text{Mn}(\text{CO})_5$	White	82–83°	70°/20	38, 102, 149
$\text{C}_2\text{F}_5\text{COMn}(\text{CO})_5$	White	49–50°	Volatile	113
$\text{C}_2\text{F}_5\text{Mn}(\text{CO})_5$	Colorless	15–17°	155°/760 (extrap.)	113
$\text{C}_2\text{F}_5\text{CRe}(\text{CO})_5$	Pale yellow	81–83°	Volatile	113
$\text{C}_2\text{F}_5\text{Re}(\text{CO})_5$	White	39–40°	Volatile	113
$n\text{-C}_3\text{F}_7\text{COMn}(\text{CO})_5$	Pale yellow	38–40°	56°/3	38, 113
$n\text{-C}_3\text{F}_7\text{Mn}(\text{CO})_5$	Colorless	~ 0°	66°/13	38, 113
$n\text{-C}_3\text{F}_7\text{CRe}(\text{CO})_5$	Pale yellow	54°	Volatile	113
$n\text{-C}_3\text{F}_7\text{Re}(\text{CO})_5$	Colorless	~ 27°	Volatile	113
$(\text{CF}_3)_2\text{CFCOMn}(\text{CO})_5$	Pale yellow	34–37°	58°/3	38
$(\text{CF}_3)_2\text{CFMn}(\text{CO})_5$	Colorless	2°	73°/17	38
$\text{HCF}_2\text{CF}_2\text{COMn}(\text{CO})_5$	White	47°	—	153
$\text{HCF}_2\text{CF}_2\text{Mn}(\text{CO})_5$	White	31°	25°/0.1	153
$\text{Cl}(\text{CF}_2)_4\text{COMn}(\text{CO})_5$	Pale yellow	39–40°	50°/2	38
$\text{Cl}(\text{CF}_2)_4\text{Mn}(\text{CO})_5$	Pale yellow	Liquid	58°/1	38
$\text{H}(\text{CF}_2)_4\text{COMn}(\text{CO})_5$	Pale yellow	22–23°	50°/13	38
$\text{H}(\text{CF}_2)_4\text{Mn}(\text{CO})_5$	Colorless	Liquid	68°/2	38
$(\text{CF}_2)_3(\text{CO})_2[\text{Mn}(\text{CO})_5]_2$	Pale yellow	105–106°	Decarbonylates on sublimation attempt	104

TABLE II—*continued*

196

Compounds	Color	M.p. (°C)	B.p. or sublimation temp. (°C/mm)	Reference
$(\text{CF}_2)_3[\text{Mn}(\text{CO})_5]_2$	White	161°	105°/0.25	104
$\text{HCFClCF}_2\text{Mn}(\text{CO})_5$	Pale yellow	43–44°	—	153
$\text{HCCl}_2\text{CF}_2\text{Mn}(\text{CO})_5$	Pale yellow	68–70°	—	153
$\text{CF}_3\text{CH}=\text{C}(\text{CF}_3)\text{Mn}(\text{CO})_5$	Yellow	Liquid	—	153
(C) $\text{RM}(\text{CO})_4\text{PR}'_3$ (M = Mn, R' = C_6H_5 , C_2H_5 , or OC_6H_5) Derivatives				
$\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$	Bright yellow	~ 101°	Subl. slowly at 80°/high vacuum	48, 49
$\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{OC}_6\text{H}_5)_3$	Bright yellow	71–72°	—	49
$\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_2\text{H}_5)_3$	Nearly colorless	Liquid	25°/high vacuum	48, 49
$\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_{11})_3$	Bright yellow	122°	—	49
$\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_{11})_3$	—	103°	—	49
$\text{CF}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_{11})_3$	—	98°	—	49
(D) $\text{R}_2\text{Fe}(\text{CO})_4$ Derivatives				
$\text{C}_4\text{F}_8\text{Fe}(\text{CO})_4$	White	77°	Subl. 25°/0.1	182
$(\text{C}_2\text{F}_5)_2\text{Fe}(\text{CO})_4$	White	62–63.5°	Subl. 25°/0.1	50
$(\text{C}_3\text{F}_7)_2\text{Fe}(\text{CO})_4$	White	88–90°	Subl. 25°/0.1	50
(E) $\text{RM}(\text{CO})_2\text{C}_5\text{H}_5$ (M = Fe, Ru) Derivatives				
$\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$	Orange	78–82°	Subl. ~ 25°/0.001	52
$\text{CH}_3\text{Ru}(\text{CO})_2\text{C}_5\text{H}_5$	White	39–40°	Subl. 40°/0.1	53
$\text{C}_2\text{H}_5\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$	Caramel	Liquid	~ 25°/0.001	52
$\text{C}_2\text{H}_5\text{Ru}(\text{CO})_2\text{C}_5\text{H}_5$	Colorless	~ –5°	Volatile	53

R. B. KING

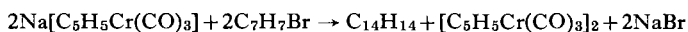
$\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$	Yellow-orange	26–30°	Volatile	52
		35°		117
$(\sigma\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$	Orange	46°	~ 50°/0.001	52
$(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	103–105°	Subl. 80°/0.1	103
$(\text{CH}_2)_4[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	123–124°	—	103
$(\text{CH}_2)_5[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	82–83°	—	103
$(\text{CH}_2)_6[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	98–100°	—	103
$\text{C}_3\text{N}_3\text{Cl}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	~ 150° (dec.)	—	103
$\text{C}_4\text{H}_4[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	—	—	103
$(\text{CH}_2)_3\text{CO}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	133–134°	—	103
$(\text{CH}_2)_3(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	110–111.5°	—	211
$(\text{CH}_2)_4(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	143–143.5°	—	211
$(\text{CF}_2)_3(\text{CO})_2[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$	Orange	112–113°	—	211
$(\text{CH}_3)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$	Orange	111–112°	80°/0.1	211
$(\text{C}_2\text{H}_5)_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$	Orange	75–76.5°	80°/0.1	211
$\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$	Orange	56–57°	70°/0.3	211
$\text{C}_6\text{H}_5\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$	Orange	60–63°	80°/0.1	117
$\text{CF}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$	Orange	33–34°	55°/0.5	117
$\text{CH}_2=\text{CHCH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$	Yellow	Liquid	45°/0.001, dec. ~ 65°	101
(F) $\text{RCo}(\text{CO})_4$ Derivatives				
$\text{CH}_3\text{Co}(\text{CO})_4$	Yellow	~ –44°	Volatile, dec. > –35°	55
$\text{C}_2\text{H}_5\text{Co}(\text{CO})_4$	—	—	Unstable	231
$\text{C}_6\text{H}_5\text{CH}_2\text{Co}(\text{CO})_4$	—	—	Unstable	231
$\text{CF}_3\text{COC}(\text{CO})_4$	Yellow	4°	Loses CO	111
$\text{CF}_3\text{Co}(\text{CO})_4$	Yellow	11°	91°/760	38, 111
$\text{C}_2\text{F}_5\text{COC}(\text{CO})_4$	Deep yellow	–33°	Unstable	112
$\text{C}_2\text{F}_5\text{Co}(\text{CO})_4$	Yellow	–30°	110°/760	38
$n\text{-C}_3\text{F}_7\text{Co}(\text{CO})_4$	Yellow	—	44°/16	38
$\text{C}_7\text{F}_{15}\text{Co}(\text{CO})_4$	Yellow	30°	—	112
$1,2\text{-C}_2\text{F}_4[\text{Co}(\text{CO})_4]_2$	Orange	80° (dec.)	25°/0.1	232

TABLE II—*continued*

Compounds	Color	M.p. (°C)	B.p. or sublimation temp. (°C/mm)	Reference
(G) $\text{RCo}(\text{CO})_3\text{PR}_3$ Derivatives				
$\text{CH}_3\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	123°	—	234
$\text{C}_2\text{H}_5\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	98–100°	—	234
$(\text{CH}_3)_2\text{CHCOCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	101°	—	234
$n\text{-C}_5\text{H}_{11}\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	95–98°	—	234
$\text{C}_6\text{H}_5\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	119–122°	—	234
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	120–130°	—	234
$p\text{-C}_6\text{H}_4(\text{CO})_2[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$	Yellow	—	—	234
$\text{CF}_3\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	170–175°	—	111, 234
$\text{CH}_3\text{OCH}_2\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	150°	—	234
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	63.5–65.5°	—	234
$\text{CH}_3\text{OOCCH}_2\text{CH}_2\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	115–117°	—	234
$\text{ClCH}_2\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	88–90°	—	234
$\text{Cl}(\text{CH}_2)_3\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	115–120°	—	234
$\text{NCCCH}_2\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	120° (dec.)	—	234
$\text{CF}_3\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Colorless	168°	—	111
$\text{CH}_3\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Canary yellow	30° (dec.)	—	56, 57
$\text{CH}_3\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$	Dirty yellow	10° (dec.)	—	56, 57
$\text{C}_2\text{F}_5\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Lemon yellow	138°	—	112
$\text{C}_2\text{F}_5\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	Yellow	145°	—	112

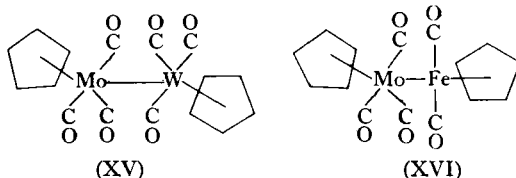
π -allyl derivative $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2$ (XIV) may be obtained in good yield as an air-stable, deep yellow, crystalline solid, m.p. 134°C (dec) which may be purified by sublimation at 35°C in high vacuum. Treatment of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2$ with a mixture of hydrogen chloride and oxygen removes the π -allyl group, producing the interesting pale yellow molybdenum oxychloride derivative $\text{C}_5\text{H}_5\text{MoO}_2\text{Cl}$ (131).

Treatment of the sodium salt $\text{Na}[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]$ with tropylium bromide does not result in a cycloheptatrienyl derivative (134). Instead, a coupling reaction occurs producing ditropyl (dicycloheptatrienyl) and $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$



This reaction represents one of the most convenient preparations of the difficultly accessible $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$.

Some interesting metal carbonyl derivatives containing two different transition metals have been prepared by reactions involving $\text{Na}[\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]$. The reaction between $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ and $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{I}$ yields red crystalline $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ (XV), m.p. 250°C (45), and the reaction between $\text{Na}[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$, red-violet crystalline $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (XVI), m.p. 209°C (135).

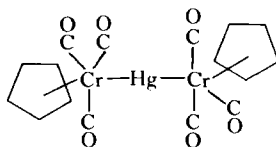


The yields in these reactions are 40–65%. From infrared spectra neither of these compounds appears to contain bridging carbonyl groups. The molybdenum-iron compound may be sublimed carefully at $110^\circ\text{C}/0.1\text{ mm}$ without decomposing into $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$. However, more vigorous sublimation conditions lead to decomposition into $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and probably also $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$.

The nitrosyl derivatives $\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{NO}$ ($\text{M} = \text{Mo}$ and W) may be obtained as orange volatile crystalline solids by treatment of the anion $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]^-$ either with nitric oxide (136) or with sodium nitrite and acetic acid (117).

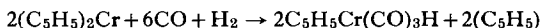
Aqueous solutions of the $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]^-$ anions give brown precipitates with $[(\text{C}_5\text{H}_5)_2\text{Co}]^+$ and yellow precipitates with mercury(II) cyanide (83). The mercury derivative $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2\text{Hg}$ is a yellow air-stable

solid sublimable at $\sim 110^\circ\text{C}/0.1\text{ mm}$ and soluble in organic solvents such as acetone or benzene to give yellow solutions. These properties are entirely consistent with those expected for the covalent derivative (XVII).



(XVII)

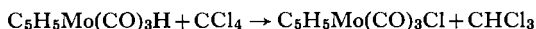
Treatment of solutions of the anions $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]^-$ with acids liberates the hydrides $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$ as yellow, volatile, air-sensitive solids (83). The stability of these hydrides to both thermal decomposition and oxidation increases in the series $\text{Cr} < \text{Mo} \ll \text{W}$. The tungsten derivative may be heated to 185°C before decomposition occurs and may be handled for short periods in the air (52). It is light-sensitive, however (83). Because these hydrides are very weak acids, even acetic acid will suffice for their liberation (52). One of the best methods of obtaining the hydrides $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}$ or W) involves treatment of tetrahydrofuran or 1,2-dimethoxyethane solutions of $\text{Na}[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]$ with glacial acetic acid, removing solvent in a vacuum, and isolating the products by sublimation from the dry residue at $\sim 50^\circ\text{C}/0.1\text{ mm}$ (52). The chromium derivative $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{H}$ may likewise be obtained by acidification of the $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]^-$ anion (83) and by reaction of biscyclopentadienylchromium with a mixture of hydrogen and carbon monoxide under pressure at 75°C (83, 130)



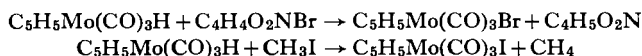
If the temperature of this system is raised above $\sim 120^\circ\text{C}$ the second cyclopentadienyl ring is removed from the $(\text{C}_5\text{H}_5)_2\text{Cr}$ to form chromium hexacarbonyl in good yield (83). A third preparation of $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{H}$ involves treatment of $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ with hydrogen at 150 atm at 70°C (83). The analogous reaction fails in the cases of the molybdenum and tungsten derivatives, presumably due to the greater strength of their metal-metal bonds.

These hydrides, especially $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$, have been used for a variety of reactions. They may be halogenated by a variety of reagents. Treatment of $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ with carbon tetrachloride gives the red-orange chloride

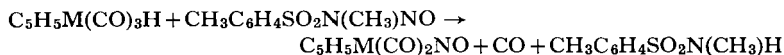
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ in good yield. The carbon tetrachloride is converted to chloroform (52)



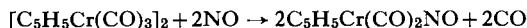
Bromination to give red $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Br}$ may be effected with *N*-bromo-succinimide in diethyl ether. Iodination to give red-black $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$ occurs with methyl iodide in refluxing benzene (52)



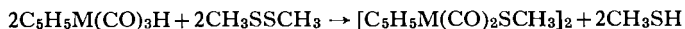
The iodide may also be obtained by treating either $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2\text{Hg}$ (52) or $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ (44) with iodine in an appropriate solvent. Treatment of $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}$ or W) with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("Diazald") gives the orange volatile nitrosyl derivatives $\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{NO}$ ($\text{M} = \text{Mo}$ or W) (52, 117)



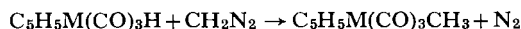
The orange chromium analog $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{NO}$ has been obtained by treatment of $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ with nitric oxide (136)



Treatment of $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}$ or W) with dimethyldisulfide gives the black to dark red crystalline methylthio derivatives $[\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{SCH}_3]_2$ ($\text{M} = \text{Mo}$ or W) (137)

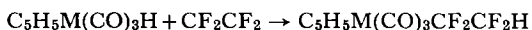


The tungsten derivative reacts at a much slower rate than the molybdenum compound, presumably due to the greater stability of the tungsten-hydrogen bond. The product obtained from this reaction between $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ and dimethyldisulfide at room temperature is of a different type than the brown crystalline $[\text{C}_5\text{H}_5\text{Mo}(\text{CH}_3\text{S})_2]_2$ obtained by heating $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ with dimethyldisulfide to $\sim 135^\circ\text{C}$ in an inert solvent (138). The hydrides $\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$ ($\text{M} = \text{Mo}$ or W) may be converted to methyl derivatives by reaction with diazomethane in ethereal solution (52, 83)



Higher yields have been obtained with the tungsten derivative (83) than with the molybdenum derivative (52). Finally, treatment of the hydrides

$C_5H_5M(CO)_3H$ ($M = Mo$ or W) with tetrafluoroethylene (139) gives the yellow crystalline derivatives $C_5H_5M(CO)_3CF_2CF_2H$ ($M = Mo$ or W) (137, 139).



VI

DERIVATIVES OF MANGANESE, TECHNETIUM, AND RHENIUM

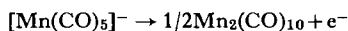
The first publications concerning anionic derivatives of manganese carbonyl were two short notes in 1957 by Closson, Kozikowski, and Coffield of the Ethyl Corporation (96). They described the use of the $[Mn(CO)_5]^-$ anion obtained from dimanganese decacarbonyl for the preparation of the alkyl and acyl derivatives $RMn(CO)_5$. The unprecedented stability of these compounds coupled with the novel and significant decarbonylation reaction characteristic of the acyl derivatives (see below) have interested a variety of investigators. Several interesting types of compounds have been obtained from $[Mn(CO)_5]^-$, mostly prepared from samples of dimanganese decacarbonyl obtained from the Ethyl Corporation, Detroit, Michigan.

Obtaining dimanganese decacarbonyl has always been somewhat of a problem. At the time the original report of the alkyl and acyl compounds by Closson *et al.* appeared, the only published method for the preparation of dimanganese decacarbonyl was the method used by Brimm and associates of Linde Air Products in their original characterization of it (123). This method involved reduction of a specially prepared manganese(II) iodide with magnesium metal in diethyl ether. An $\sim 1\%$ yield of $Mn_2(CO)_{10}$ could be obtained by this method if one were fortunate! An extensive program of research by the Ethyl Corporation has resulted in several somewhat more efficient preparations of dimanganese decacarbonyl. These include, in approximately increasing order of ease and efficiency, the reduction of manganese halides with Grignard reagents in the presence of carbon monoxide under carefully controlled conditions (9% yield) (140), the treatment of the reaction product of manganese(II) chloride and sodium benzo-phenone ketyl with carbon monoxide under pressure in tetrahydrofuran solution (30% yield) (141), the reduction of manganese(II) acetate with alkyl-aluminium compounds in diethyl ether in the presence of carbon monoxide

under pressure (55% yield) (142), and the reduction of methylcyclopentadienylmanganese tricarbonyl with sodium dispersion in diglyme in the presence of carbon monoxide under pressure (50% yield but avoids the use of the pyrophoric alkylaluminum compounds) (64). Despite these improved methods dimanganese decacarbonyl remains among the rarest of the carbonyl derivatives of the 3*d* transition metals, as illustrated by the prices, effective in January, 1963, of some of these carbonyls from major corporations: chromium hexacarbonyl, \$150 per pound (Ethyl Corporation); dimanganese decacarbonyl, \$400 per pound (Ethyl Corporation); iron pentacarbonyl, \$1.50 per pound (Antara Division of General Aniline and Film); and dicobalt octacarbonyl, \$25 per pound (Union Carbide).

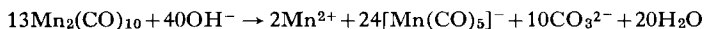
The corresponding carbonyl derivatives of technetium and rhenium form similar anions $[M(CO)_5]^-$, which as far as has been determined, form similar derivatives. Although the carbonyls $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ may be relatively easily obtained by action of carbon monoxide under pressure on the oxides TcO_2 (45) or Tc_2O_7 (143, 144) and Re_2O_7 (145), the relative rarity of rhenium and technetium more than compensates for the ease of preparation of their carbonyls. For this reason, dimanganese decacarbonyl, despite its high price, is still more available and less expensive than the carbonyls of technetium and rhenium. Technetium, the only manmade element discussed in this chapter, in fact, is so expensive (\sim \$100 per gram for per-technetates in 1962) that most research groups recover it carefully from reaction residues!

The carbonyls $M_2(CO)_{10}$ may be converted to the sodium salts of the anions $[M(CO)_5]^-$ by reduction with dilute sodium amalgam in ethereal solvents, especially tetrahydrofuran. In the case of manganese the yellow color of the carbonyl is soon discharged by the sodium amalgam (5), leaving a nearly colorless solution containing gray particles of suspended mercury. From this solution the solid sodium salt may be isolated as an almost colorless very air-sensitive powder (5). A potential of -0.68 volt (5) has been determined for the reaction



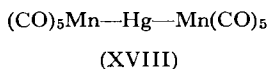
In the cases of rhenium (47) and more especially technetium (45) the reduction of the carbonyls in tetrahydrofuran solution, besides forming the colorless or yellow anions $[M(CO)_5]^-$, produces an unknown red species, as indicated by the color of the reduced solution. The sodium salt $Na[Re(CO)_5]$ has been isolated in the pure state as a yellow air-sensitive powder (47).

Alternative methods are available for the preparation of $[\text{Mn}(\text{CO})_5]^-$. A convenient method is the reaction of dimanganese decacarbonyl with hydroxide ion (146)

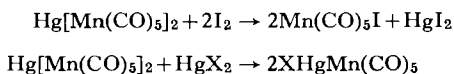


One disadvantage of this method is the loss of $\sim 7\%$ of the manganese of the dimanganese decacarbonyl as Mn^{2+} . A more serious objection is the presence of the strongly basic solution in which many of the halides of interest for reaction with $[\text{Mn}(\text{CO})_5]^-$ are not stable. Nevertheless, the use of alcoholic potassium hydroxide to generate $[\text{Mn}(\text{CO})_5]^-$ from $\text{Mn}_2(\text{CO})_{10}$ is the basis for a convenient preparation of $\text{CH}_3\text{Mn}(\text{CO})_5$ (93). Although Hieber and Wagner (5, 93) report that the reaction between dimanganese decacarbonyl and alcoholic potassium hydroxide proceeds at room temperature, King (117) has found elevated temperatures necessary for satisfactory results. In addition, in certain reactions of dimanganese decarbonyl with nitrogen bases (12, 13) discussed above, $[\text{Mn}(\text{CO})_5]^-$ is produced. However, the loss of one-third of the manganese as $[\text{Mn}(\text{base})_6]^{2+}$ and the possible side reaction involving the nitrogen base and the material to be reacted with the $[\text{Mn}(\text{CO})_5]^-$ anion make this reaction less suitable for obtaining $[\text{Mn}(\text{CO})_5]^-$ for preparative purposes. Finally, $[\text{Mn}(\text{CO})_5]^-$ is probably an intermediate in the preparation of dimanganese decacarbonyl from methylcyclopentadienylmanganese tricarbonyl, sodium, and carbon monoxide in diglyme solution (64).

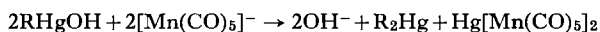
Some ionic and covalent derivatives of $[\text{Mn}(\text{CO})_5]^-$ with heavy metals have been obtained. Treatment of an aqueous solution of $\text{Na}[\text{Mn}(\text{CO})_5]$ with aqueous mercury(II) cyanide or mercury(II) sulfate yields yellow sparingly soluble $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ (146) (XVIII)



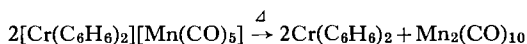
which may be purified by sublimation at $100^\circ\text{C}/0.1\text{ mm}$ (36). This mercury derivative $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ is cleaved by iodine to give $\text{Mn}(\text{CO})_5\text{I}$ and HgI_2 and reacts with mercury(II) halides in acetone solution to give the yellow compounds $\text{XHgMn}(\text{CO})_5$ (146)



Treatment of $[\text{Mn}(\text{CO})_5]^-$ with an alkylmercuric hydroxide gives a mixture of $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ and dialkylmercury, the intermediate $\text{RHgMn}(\text{CO})_5$ apparently decomposing as rapidly as it is formed (146)



Insoluble precipitates are obtained by treatment of solutions of $[\text{Mn}(\text{CO})_5]^-$ with the cations $[\text{Fe}(o\text{-phen})_3]^{2+}$, $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+$, and $[\text{Co}(\text{C}_5\text{H}_5)_2]^+$. On attempted sublimation in high vacuum the dibenzenechromium(I) salt undergoes an internal oxidation-reduction reaction, producing a mixed sublimate of dibenzene-chromium and dimanganese decacarbonyl



The $[\text{Co}(\text{C}_5\text{H}_5)_2]^+$ salt, however, may be sublimed unchanged at $160\text{--}180^\circ\text{C}$ 10^{-4} mm (146).

Of particular interest are the hydrides $\text{HM}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Tc}, \text{Re}$) obtained by acidification of the corresponding $[\text{M}(\text{CO})_5]^-$ anions. Phosphoric acid is especially convenient due to its lack of volatility and oxidizing power. Unlike $\text{HCo}(\text{CO})_4$ and $\text{HV}(\text{CO})_6$, $\text{HMn}(\text{CO})_5$, a malodorous, light- and air-sensitive, colorless liquid, is a *weak* acid ($K = 0.8 \times 10^{-7}$) and stable at $\sim +100^\circ\text{C}$ (5). Its volatility is very similar to that of the isoelectronic iron pentacarbonyl (5). Alternative preparations of $\text{HMn}(\text{CO})_5$ involve the reaction of $\text{Mn}_2(\text{CO})_{10}$ with a mixture of hydrogen and carbon monoxide at 250 atm and 200°C and the reduction of $\text{Mn}_2(\text{CO})_{10}$ with magnesium metal in an aqueous methanolic hydrochloric acid medium (5). Manganese pentacarbonyl hydride reacts with iodine or oxygen to form $\text{Mn}_2(\text{CO})_{10}$ (5). Uses of $\text{HMn}(\text{CO})_5$ to prepare other manganese carbonyl derivatives will be described below.

The rhenium analog, $\text{HRe}(\text{CO})_5$, may be obtained by treatment of $\text{Na}[\text{Re}(\text{CO})_5]$ not only with phosphoric acid but also with water (46, 47). Rhenium pentacarbonyl hydride is a colorless liquid readily oxidized by air to $\text{Re}_2(\text{CO})_{10}$. It possesses acidic character so weak that it is *not* converted to salts of $[\text{Re}(\text{CO})_5]^-$ by bases in aqueous solution—hence its preparation by treatment of $[\text{Re}(\text{CO})_5]^-$ salts with pure water. Like $\text{HMn}(\text{CO})_5$, $\text{HRe}(\text{CO})_5$ is stable at room temperature but is decomposed quantitatively to $\text{Re}_2(\text{CO})_{10}$ and hydrogen at 100°C over a period of 24 hr (47).

The technetium analog, $\text{HTc}(\text{CO})_5$, is obtained only in very low yield by acidification of the reduction product of ditechneium decacarbonyl with sodium amalgam (45). A more predominant product of this reaction is a light tan crystalline solid tentatively formulated as $\text{Tc}_3(\text{CO})_{12}$ (147). This

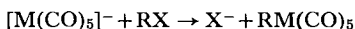
formulation, containing an odd number of electrons, is in discord with the observed diamagnetism. This trinuclear derivative, in order to account for its magnetic properties, may actually be $\text{HTc}_3(\text{CO})_{12}$ or, less likely, $\text{H}_3\text{Tc}_3(\text{CO})_{12}$ or $\text{HCTc}_3(\text{CO})_{12}$. These additional ligands, especially a single hydrogen atom, would have a very minor effect on the elemental analyses. The mononuclear $\text{HTc}(\text{CO})_5$ has been identified by comparison of its infrared spectrum with that of the manganese and rhenium compounds (45).

Some tertiary phosphine-substituted manganese carbonyl anions have also been prepared. Due to the strong metal-carbon monoxide bond in $[\text{Mn}(\text{CO})_5]^-$ such compounds cannot be prepared by reactions of $[\text{Mn}(\text{CO})_5]^-$ with tertiary phosphines (49). However, reduction of $[\text{Mn}(\text{CO})_4\text{PR}_3]_n$ (R = phenyl, $n = 1$; R = ethyl, $n = 1$; R = cyclohexyl, $n = 2$; R = phenoxy, $n = 2$) with sodium amalgam in tetrahydrofuran or, less conveniently, dimethyl ether solution gives the extremely air-sensitive yellow salts $\text{Na}[\text{Mn}(\text{CO})_4\text{PR}_3]$ (48, 49). The starting materials may be obtained by heating dimanganese decacarbonyl with the appropriate tertiary phosphine derivative (148). The rate of reduction for the substituted derivatives appears to be slower than that for dimanganese decacarbonyl itself. The lithium and magnesium salts of the triphenylphosphine derivative have also been prepared by reduction of $\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ with the appropriate amalgam.

The anions $[\text{Mn}(\text{CO})_4\text{PR}_3]^-$ form precipitates when aqueous solutions are treated with solutions of the $[\text{Ni}(o\text{-phen})_3]^{2+}$ ion (48). Treatment with mercuric cyanide gives the bright yellow mercury derivatives $\text{Hg}[\text{Mn}(\text{CO})_4\text{PR}_3]_2$, substitution products of $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ (49). As might be expected the triethylphosphine derivative $\text{Hg}[\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]_2$ is much more soluble in organic solvents than the sparingly soluble triphenylphosphine derivative $\text{Hg}[\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]_2$.

Treatment of the sodium salts $\text{Na}[\text{Mn}(\text{CO})_4\text{PR}_3]$ with phosphoric acid gives the colorless to bright yellow hydrides $\text{HMn}(\text{CO})_4\text{PR}_3$ (48, 49). The volatility of these hydrides is dependent on the size of the alkyl groups attached to the phosphorus atom. Thus, the triethylphosphine derivative, an extremely air-sensitive liquid, may be distilled at $65\text{--}70^\circ\text{C}$ in high vacuum. The triphenylphosphine and tricyclohexylphosphine derivatives, both solids, are reported to sublime at 80° and 140°C , respectively, in high vacuum. $\text{HMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ is chlorinated by carbon tetrachloride to form $\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$ (49), also prepared from $\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ and chlorine or carbon tetrachloride. Analogous bromides and iodides may also be prepared.

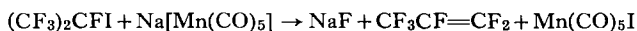
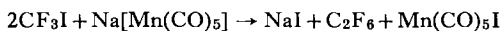
A particularly important reaction of the anions $[M(CO)_5]^-$ is the reaction with a variety of organic halides to form compounds of the general formula $RM(CO)_5$ containing a carbon-metal σ bond



(M = manganese or rhenium; no technetium compounds of this type have been reported as of June, 1963, no doubt due to the rarity of technetium). There are three factors determining whether a given organic halide will react with $[Mn(CO)_5]^-$ or $[Re(CO)_5]^-$ to form an $RM(CO)_5$ derivative.

(1) *Reactivity of the halogen atom.* No successful reaction of a phenyl or vinyl halide with $Na[Mn(CO)_5]$ or the rhenium analog to form an $RM(CO)_5$ derivative has been reported. It appears that the halogen atoms on halides of these types are too inert. Therefore, the first requirement that an organic halide react with the $[M(CO)_5]^-$ anion to form an $RM(CO)_5$ compound is that its halogen atom be sufficiently reactive.

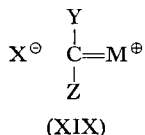
(2) *Negative or positive character of the halogen atom.* Perfluoroalkyl iodides react with $Na[Mn(CO)_5]$ to form exclusively $Mn(CO)_5I$ rather than $R_fMn(CO)_5$ (38, 149)



This is no doubt a consequence of the fact that the iodine atom in perfluoroalkyl iodides is positive and the perfluoroalkyl group negative due to the strong inductive effect of the fluorine atoms. Thus, the second requirement that an organic halide react with the $[M(CO)_5]^-$ anion to form an $RM(CO)_5$ compound is that its halogen atom be more negative than the organic group to which it is bonded. If the halogen atom is more positive than the organic group to which it is bonded, the pentacarbonyl halides $M(CO)_5X$ rather than $RM(CO)_5$ compounds will result.

(3) *Stability of the metal-carbon bond in the product.* Compounds of the type $RM(CO)_5$ where R is a secondary or tertiary alkyl group appear to be very unstable. For this reason reactions between $Na[Mn(CO)_5]$ and secondary or tertiary alkyl halides yield $Mn_2(CO)_{10}$ and hydrocarbons rather than $RMn(CO)_5$ compounds. Likewise, treatment of $Na[Mn(CO)_5]$ with tropylium bromide gives ditropyl and $Mn_2(CO)_{10}$ (150), the manganese-carbon bond in the unknown σ -cycloheptatrienyl derivative $C_7H_7Mn(CO)_5$ apparently being very unstable. In general, the stability of transition

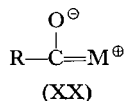
metal-carbon bonds appears to be enhanced by the presence of negative substituents on the carbon atom, possibly because of the ability of such substituents to favor resonance structures such as (XIX), thereby increasing the metal-carbon bond order through partial $p\pi-d\pi$ bonding, and removing negative charge from the metal atom.



Conversely, positive substituents decrease the stability of transition metal-carbon bonds by lessening the stability of resonance structures such as (XIX). The cycloheptatrienyl group cited above is perhaps the extreme example of a positively substituted group since the carbon atom bonded to the metal atom is a portion of a triply unsaturated seven-membered ring, which tends to take on a full positive charge as in the tropylium ion in order to possess the desired aromatic sextet.

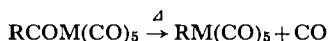
It is thus apparent that these three factors severely limit the halides which react with $[\text{Mn}(\text{CO})_5]^-$ to form $\text{RM}(\text{CO})_5$ derivatives. Methyl and benzyl halides (93, 96, 151) react especially smoothly with $[\text{Mn}(\text{CO})_5]^-$ and $[\text{Re}(\text{CO})_5]^-$ to form $\text{RM}(\text{CO})_5$. The reaction products of $\text{Na}[\text{Mn}(\text{CO})_5]$ with allyl (99, 100), perfluoroallyl (38, 99), and 1,3-trimethylene (104) halides also apparently give products of the $\text{RMn}(\text{CO})_5$ type. However, the perfluoroallyl and trimethylene derivatives have unexpected structures and the allyl derivative is easily converted to π -allylmanganese tetracarbonyl.

Although relatively few alkyl halides react with $[\text{M}(\text{CO})_5]^-$ to form straightforward $\text{RM}(\text{CO})_5$ derivatives, almost all *acyl* chlorides, RCOCl , react with $[\text{M}(\text{CO})_5]^-$ to form the acyl derivatives $\text{RCOM}(\text{CO})_5$. Approximately fifteen acyl derivatives of manganese alone have been reported. Acyl derivatives of transition metals such as these manganese compounds appear to be especially stabilized by resonance structures such as (XX), in which the metal-carbon bond has appreciable double bond character, as in the metal carbonyls themselves. The rarity and instability of acyl derivatives of non-transition metals such as tin especially emphasizes the importance of structures analogous to (XX) in stabilizing acyl derivatives of transition metals.



In addition to acyl chlorides of the usual type, the acid chloride of cyanuric acid $C_3N_3Cl_3$ reacts with $NaMn(CO)_5$ to form an acyl derivative $C_3N_3Cl[Mn(CO)_5]_2$ (104). In this reaction only two of the three available chlorine atoms are replaced by manganese pentacarbonyl residues.

Of particular interest is the tendency for these numerous acyl derivatives of manganese and rhenium to undergo facile decarbonylation on heating to form the corresponding alkyl derivatives

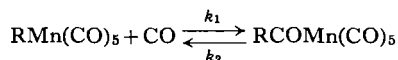


This reaction permits the preparation of many aryl and perfluoroalkyl derivatives of manganese and rhenium not obtainable by reaction of $[M(CO)_5]^-$ with halides. Thus the phenyl derivatives $C_6H_5Mn(CO)_5$ (96, 102, 152) and $C_6H_5Re(CO)_5$ (151) and the *p*-tolyl derivative $CH_3C_6H_4Mn(CO)_5$ (149) may be prepared easily by the decarbonylation of the corresponding benzoyl and toluoyl derivatives. In addition, a variety of perfluoroalkyl derivatives $R_fMn(CO)_5$ [$R_f = CF_3$ (38, 102, 149), C_2F_5 (113), *n*- C_3F_7 (113, 38), $(CF_2)_2CF$ (38), HCF_2CF_2 (153), $Cl(CF_2)_4$ (38), and $H(CF_2)_4$ (38)] and $R_fRe(CO)_5$ (113) ($R_f = C_2F_5$ and C_3F_7) have been prepared by decarbonylation of the corresponding perfluoroacyl derivatives at 90–110° C. The perfluorotrimethylene derivative $(CO)_5Mn(CF_2)_3Mn(CO)_5$ has been prepared by the decarbonylation of the perfluoroglutaryl derivative $(CO)_5MnCO(CF_2)_3COMn(CO)_5$ at 105° C (104). These perfluoroalkyl derivatives are characterized by unusual stability, undoubtedly due to the enhancement of resonance structures related to (XIX) by the highly electronegative fluorine and fluorocarbon substituents on the carbon atom bonded to the metal atom. Resonance structures such as (XIX) while stabilizing the metal-carbon bond, weaken the carbon-fluorine bond. It is therefore not surprising that fluorocarbon-transition metal derivatives such as those of manganese and rhenium are readily decomposed by bases with liberation of fluoride ion (153).

Certain aspects of the decarbonylation of acylmanganese pentacarbonyl derivatives have been studied in greater detail. Studies with labeled carbon monoxide have demonstrated that the molecule of carbon monoxide which is lost does not come from the acyl carbonyl group but instead from one of the carbonyl groups bonded to the metal atom (102). The acyl carbonyl group is changed to a metal carbonyl group during the decarbonylation reaction. The decarbonylation reaction is therefore not to be visualized as the "popping out" of the acyl carbonyl group, as may have been naively

suspected originally. Instead, it appears to be migration of the organic group attached to the acyl carbonyl group to the metal atom with concomitant displacement of one of the carbonyl groups attached to the metal atom. Therefore, the ease of decarbonylation will depend on the strength of the bond between the transition metal atom and one of the metal carbonyl groups.

The decarbonylation of acyl derivatives of manganese is reversible in many cases. Methylmanganese pentacarbonyl reacts with carbon monoxide under pressure at room temperature to form acetylmanganese pentacarbonyl in good yield (96). Calderazzo and Cotton (154) have demonstrated this carbonylation reaction of methylmanganese pentacarbonyl to be first order in both methylmanganese pentacarbonyl and carbon monoxide concentrations. In a further study Calderazzo and Cotton (155) have investigated the dependence of the equilibrium constants k_1 and k_2 for the carbonylation and decarbonylation reactions on the nature of the alkyl group. In this case k_1 and k_2 represent the rates of the carbonylation and decarbonylation reactions, respectively



The constant k_1 was found to decrease in the series $\text{R} = n\text{-C}_3\text{H}_7 > \text{C}_2\text{H}_5 > \text{C}_6\text{H}_5 > \text{CH}_3 \gg \text{C}_6\text{H}_5\text{CH}_2, \text{CF}_3$. It thus appears that electronegative substituents favor the decarbonylation reaction over the carbonylation reaction. This may arise from the tendency for such substituents on the acyl group to withdraw electrons to a greater extent from the metal atom, leaving a lower electron density on the metal atom to participate in partial double-bonding with the carbon monoxide ligands. Thus the bonding between the metal atom and the carbon monoxide ligands is weakened. This weakening would be expected to facilitate the decarbonylation reaction since, as indicated above, the molecule of carbon monoxide which is lost comes from one of the metal carbonyl groups rather than from the acyl carbonyl group.

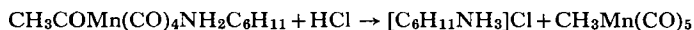
These kinetic observations of Calderazzo and Cotton concerning the carbonylation-decarbonylation reaction are consistent with observations of other workers. For example, Coffield *et al.* (102) reported that the trifluoromethyl derivative $\text{CF}_3\text{Mn(CO)}_5$ could not be carbonylated to the trifluoroacetyl derivative $\text{CF}_3\text{COMn(CO)}_5$. In addition, the material, m.p. 58°C , obtained from $\text{Na[Mn(CO)}_5]$ and ethyl iodide and originally thought to be ethylmanganese pentacarbonyl (93), was later demonstrated to be the propionyl derivative $\text{C}_2\text{H}_5\text{COMn(CO)}_5$ (151). The carbonylation reaction is

apparently so facile that carbon monoxide liberated during the decomposition of some of the ethylmanganese pentacarbonyl is able to carbonylate some of the remaining ethylmanganese pentacarbonyl to the propionyl derivative.

Alkylmanganese pentacarbonyl derivatives, besides reacting with carbon monoxide to form acylmanganese pentacarbonyl derivatives, may react similarly with other electron pair-donating ligands to form substituted acylmanganese carbonyl derivatives



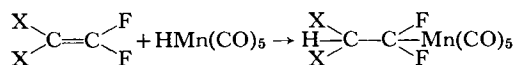
In this case the metal carbonyl group displaced by the ligand becomes an acyl carbonyl group. Reactions of this type have been demonstrated for ammonia, cyclohexylamine, *N*-methylcyclohexylamine, and aniline on $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_5$ (152). Treatment of $\text{CH}_3\text{COMn}(\text{CO})_4\text{NH}_2\text{C}_6\text{H}_{11}$ with hydrogen chloride removes the amine as its hydrochloride, giving methylmanganese pentacarbonyl (152)



This reaction is somewhat similar to the decarbonylation reaction except that an amine ligand is removed by salt formation with acid rather than a carbon monoxide ligand as very volatile free carbon monoxide.

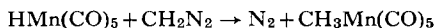
Syntheses of $\text{RM}(\text{CO})_5$ compounds by reaction of $[\text{M}(\text{CO})_5]^-$ with halides or by decarbonylation of acyl derivatives have been described. A third synthesis involves treatment of the pentacarbonyl halides $\text{M}(\text{CO})_5\text{X}$ with an organic derivative of lithium or magnesium. Examples of this reaction include the treatment of $\text{Mn}(\text{CO})_5\text{Br}$ with benzylmagnesium chloride to give the benzyl derivative $\text{C}_6\text{H}_5\text{CH}_2\text{Mn}(\text{CO})_5$ (93) and the reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with phenyllithium to give the phenyl derivative $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_5$ (156). Disadvantages of reactions of this type include the formation of much $\text{Mn}_2(\text{CO})_{10}$ as a by-product and a low yield of the desired product.

Reactions involving $\text{HMn}(\text{CO})_5$ have also been of use in synthesizing $\text{RMn}(\text{CO})_5$ derivatives, especially when the R group has several fluorine substituents. Fluoroolefins of general formula $\text{X}_2\text{C}=\text{CF}_2$ add to manganese carbonyl hydride to form $\text{HX}_2\text{CCF}_2\text{Mn}(\text{CO})_5$, the addition reaction occurring in such a manner that the CF_2 group is adjacent to the manganese atom (153)



This reaction occurs readily under pressure at room temperature and has been successfully accomplished for tetrafluoroethylene, chlorotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene. $\text{HCF}_2\text{CF}_2\text{Mn}(\text{CO})_5$ has also been synthesized by the decarbonylation of the acyl derivative $\text{HCF}_2\text{CF}_2\text{COMn}(\text{CO})_5$ (153). Reaction of $\text{HMn}(\text{CO})_5$ with hexafluorobutyne-2 gives $\text{CF}_3\text{CH}=\text{C}(\text{CF}_3)\text{Mn}(\text{CO})_5$.

Another reaction of interest is that of $\text{HMn}(\text{CO})_5$ with diazomethane in ethereal solution (5, 93)



This reaction is much less convenient and less efficient than the synthesis of $\text{CH}_3\text{Mn}(\text{CO})_5$ from $[\text{Mn}(\text{CO})_5]^-$ and methyl iodide.

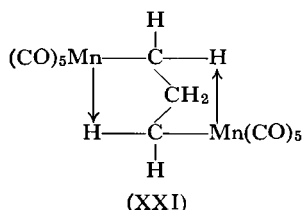
The reaction between perfluoroallyl chloride and $\text{Na}[\text{Mn}(\text{CO})_5]$ leads to a white crystalline solid, m.p. $\sim 75^\circ\text{C}$, of the expected composition $\text{C}_3\text{F}_5\text{Mn}(\text{CO})_5$ (38, 113). F^{19} NMR studies have shown this compound to be σ -perfluoropropenylmanganese pentacarbonyl, $\text{CF}_3\text{CF}=\text{CFMn}(\text{CO})_5$, rather than the expected perfluoroallylmanganese pentacarbonyl, $\text{CF}_2=\text{CF}-\text{CF}_2\text{Mn}(\text{CO})_5$.

These $\text{RM}(\text{CO})_5$ compounds are white to pale yellow liquids or solids melting below 100°C . They are very volatile. Crystals of $\text{CH}_3\text{Mn}(\text{CO})_5$, for example, evaporate when placed in an open container (93). Most of these compounds, especially the acyl and perfluoroalkyl derivatives, which have electronegative substituents on the carbon atom bonded to the manganese atom, are indefinitely stable in air.

The anions $[\text{Mn}(\text{CO})_4\text{PR}_3]^-$, like the unsubstituted derivative, react with methyl iodide to form the bright yellow methyl derivatives $\text{CH}_3\text{Mn}(\text{CO})_4\text{PR}_3$ (48, 49) (R = phenyl, ethyl, cyclohexyl, or phenoxy). The phenyl, phenoxy, and cyclohexyl derivatives are solids and the ethyl derivative a liquid. The phenyl and ethyl derivatives have been sublimed or distilled at $\sim 80^\circ\text{C}$ in high vacuum. The compounds $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_{11})_3$ and $\text{CF}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_{11})_3$ have also been prepared.

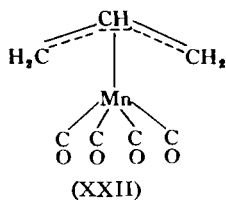
Reaction between 1,3-dibromopropane or $\text{Cl}(\text{CH}_2)_3\text{COCl}$ and $\text{Na}[\text{Mn}(\text{CO})_5]$ has been found to yield a bright yellow crystalline solid of the composition $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ (104). The proton NMR spectrum, unlike that of 1,3-dibromopropane itself or of the iron complex $(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$, exhibits three resonances of relative intensities 1 : 1 : 1. This NMR spectrum cannot be explained on the basis of the structure $(\text{CO})_5\text{MnCH}_2\text{CH}_2\text{CH}_2\text{Mn}(\text{CO})_5$, where manganese pentacarbonyl residues are simply σ -bonded to

each end of the three-carbon chain. In order to account for this NMR spectrum, a novel structure (XXI) with an unprecedented type of manganese–hydrogen bond has been proposed. This manganese–hydrogen bond



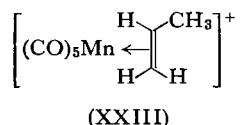
may be regarded as formed by the partial donation of one of the three unbonded electron pairs in the d orbitals to the relatively positive hydrogen atom. It thus resembles the hydrogen bond in the HF_2^- ion, where one of the three lone electron pairs of the fluorine atom is donated to the relatively positive hydrogen atom. The manganese–hydrogen bond present in the proposed structure for $(\text{CH}_2)_3[\text{Mn}(\text{CO})_5]_2$ is thus entirely different from the manganese–hydrogen bond in $\text{HMn}(\text{CO})_5$ and similar compounds, where one electron arises from the hydrogen atom and one electron from the manganese atom. Unfortunately, neither X-ray nor neutron diffraction data are yet available on this unusual compound. The failure of this structural feature to occur in simpler compounds may arise from the fact that each of the two unusual manganese–hydrogen bonds in (XXI) is part of a five-membered ring consisting of three carbon atoms, one hydrogen atom, and one manganese atom. Formation of a chelate-type of ring may thus be necessary for the formation of a bond of this type. A similar compound of composition $\text{CH}_3\text{C}_3\text{H}_5[\text{Mn}(\text{CO})_5]_2$ has been obtained from 1,3-dibromobutane and $\text{Na}[\text{Mn}(\text{CO})_5]_2$ (104).

Reaction of $\text{Na}[\text{Mn}(\text{CO})_5]$ with allyl chloride yields the yellow air-sensitive liquid $\text{CH}_2=\text{CHCH}_2\text{Mn}(\text{CO})_5$ with an allyl group σ -bonded to a manganese pentacarbonyl residue in the usual manner (99, 100). Heating this allylmanganese pentacarbonyl derivative to $80\text{--}90^\circ\text{C}$ causes it to lose one mole of carbon monoxide to form π -allylmanganese tetracarbonyl (XXII), a yellow volatile crystalline solid, m.p. $52\text{--}53.5^\circ\text{C}$ (99, 100). Similar



syntheses have been carried out with the substituted allylic halides $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$, and $\text{ClCH}=\text{CHCH}_2\text{Cl}$, the resulting π -allylmanganese tetracarbonyl derivatives being liquid at room temperature (100). In an alternative synthesis of π -allylmanganese tetracarbonyl derivatives $\text{HMn}(\text{CO})_5$ is added to the dienes $\text{CH}_2=\text{CRCH}=\text{CH}_2$ ($\text{R} = \text{H}, \text{CH}_3, \text{Cl}$). The initially formed substituted σ -allylmanganese pentacarbonyl derivative may be readily decarbonylated on heating to form the corresponding π -allylmanganese tetracarbonyl derivative (100).

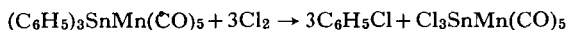
The protonation of σ -allylmanganese pentacarbonyl by perchloric acid to form salts of the π -propenemanganese pentacarbonyl cation (XXIII) has been briefly described (132).



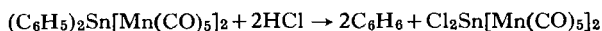
Several compounds with an $\text{Mn}(\text{CO})_5$ residue σ -bonded to elements other than carbon have been described. Treatment of $\text{Na}[\text{Mn}(\text{CO})_5]$ with triphenylchlorosilane yields scarlet $(\text{C}_6\text{H}_5)_3\text{SiMn}(\text{CO})_5$ containing a silicon-manganese bond (157). An analogous reaction between $\text{Na}[\text{Mn}(\text{CO})_5]$ and triphenylbromogermane yields white crystalline $(\text{C}_6\text{H}_5)_3\text{GeMn}(\text{CO})_5$ containing a germanium-manganese bond (158). Tin and lead derivatives of the types $\text{R}_2\text{E}[\text{Mn}(\text{CO})_5]_2$ and $\text{R}_3\text{EMn}(\text{CO})_5$ ($\text{R} = \text{phenyl, methyl, or ethyl}$; $\text{E} = \text{tin or lead}$) have also been obtained by reaction between $\text{Na}[\text{Mn}(\text{CO})_5]$ and the corresponding halides (157). The stability of these compounds appears to increase in the series $\text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$. As the number of $\text{Mn}(\text{CO})_5$ groups increases in a given series of compounds the stability to oxidation decreases.

Several reactions of interest have been carried out with the triphenyltin derivative $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$. Heating this compound with triphenylphosphine causes the replacement of one mole of carbon monoxide with triphenylphosphine to form the white substitution product $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ (157), also prepared from $\text{Na}[\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ and $(\text{C}_6\text{H}_5)_3\text{SnCl}$. Triphenylarsine gives a similar derivative, $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3$. Treatment of $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ with tetraphenylcyclopentadienone causes the replacement of two moles of carbon monoxide to form the π complex $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_3(\text{tetracyclone})$ (XXIV) (157). Of particular interest is the reaction between chlorine and $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$,

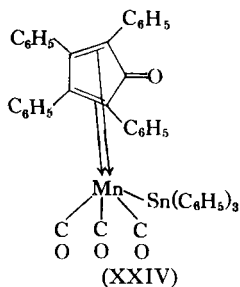
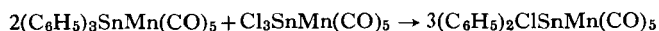
where the tin–carbon bond rather than the tin–manganese bond is broken, forming $\text{Cl}_3\text{SnMn}(\text{CO})_5$



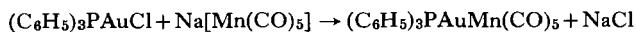
This reaction demonstrates the great stability of the tin–manganese bond. This is in agreement with very recent work which demonstrates the stability of bonds between tin and other transition metals such as platinum (159), rhodium (160), and iridium (161). In another cleavage reaction $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ reacts with HCl to form $\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ (157)



Finally, a symproportionation reaction of the Kocheskov type may be carried out between $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ and $\text{Cl}_3\text{SnMn}(\text{CO})_5$ to produce the “mixed” derivative $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$



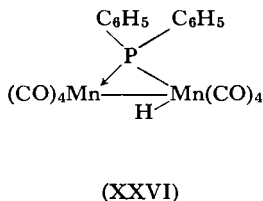
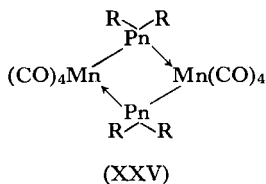
$\text{Hg}[\text{Mn}(\text{CO})_5]_2$, with manganese–mercury bonds, is obtained from $[\text{Mn}(\text{CO})_5]^-$ and mercury(II) cyanide and has already been discussed. A very stable compound with a manganese–gold bond has been obtained by the reaction between $\text{Na}[\text{Mn}(\text{CO})_5]$ and $(\text{C}_6\text{H}_5)_3\text{PAuCl}$ (162)



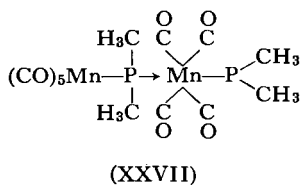
Compounds containing a manganese atom bonded to another transition metal have also been obtained by use of $\text{Na}[\text{Mn}(\text{CO})_5]$. For example, treatment of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ with $\text{Na}[\text{Mn}(\text{CO})_5]$ yields $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Mn}(\text{CO})_5$, with an iron–manganese bond, as a red volatile crystalline solid, m.p. 76°C (135). Treatment of $\text{C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{I}$ with $\text{Na}[\text{Mn}(\text{CO})_5]$ yields $\text{C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{Mn}(\text{CO})_5$, with a molybdenum–manganese bond, as a dark green volatile crystalline solid, m.p. 123°C (dec) (117). Similarly, the “pure” carbonyl derivative, manganese rhenium decacarbonyl, MnRe

(CO)₁₀, has recently been obtained in 60% yield as yellow crystals, m.p. 167° C, by reaction between NaMn(CO)₅ and Re(CO)₅Cl (163). It is also obtained in the "inverse" reaction between Mn(CO)₅Br and NaRe(CO)₅. The iron-manganese compound is reported to form the water-stable red cation [C₅H₅Fe(CO)₂Mn(CO)₅H]⁺ on protonation with strong acid (164). This cation may be isolated as the red hexafluorophosphate salt.

Some interesting compounds have been obtained by treatment of Na[Mn(CO)₅] with R₂PnCl (R = methyl or phenyl; Pn = phosphorus or arsenic). Green and Moelwyn-Hughes (165) have described the reaction between Na[Mn(CO)₅] and (C₆H₅)₂PCl to give mainly the yellow, air-stable, nonvolatile [(C₆H₅)₂PMn(CO)₄]₂ of structure (XXV; Pn = P, R = C₆H₅).

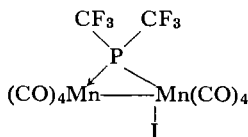


In this reaction a yield of up to 2% of a yellow somewhat air-sensitive crystalline solid which sublimes at 160° C in high vacuum was reported. This was formulated by Green and Moelwyn-Hughes (165) as (C₆H₅)₂PMn₂(CO)₈H (XXVI). Hayter (166) has investigated reactions of this type in greater detail. Treatment of Na[Mn(CO)₅] with (CH₃)₂PCl produces initially [(CH₃)₂P]₂Mn₂(CO)₉, to which structure (XXVII), containing one



bridging (CH₃)₂P group and one terminal (CH₃)₂P group, was assigned. Heating this compound in boiling toluene solution causes the loss of one mole of carbon monoxide to form the octacarbonyl derivative [(CH₃)₂PMn(CO)₄]₂ (XXV; Pn = P; R = CH₃), also obtainable by refluxing Mn₂(CO)₁₀ with tetramethylbiphosphine in toluene. The similar compounds [(C₆H₅)₂AsMn(CO)₄]₂ (XXV; Pn = As, R = C₆H₅) (167) and

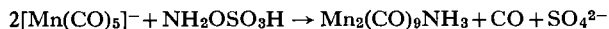
$\text{Mn}_2(\text{CO})_8\text{P}(\text{CF}_3)_2\text{I}$ (XXVIII) (168) have been obtained by refluxing $\text{Mn}_2(\text{CO})_{10}$ with solutions of $(\text{C}_6\text{H}_5)_3\text{As}$ and $(\text{CF}_3)_2\text{PI}$, respectively.



(XXVIII)

Treatment of $\text{HMn}(\text{CO})_5$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("Diazald") in ether solution at room temperature gives the nitrosyl derivative $\text{Mn}(\text{CO})_4\text{NO}$ as an unstable dark red liquid, m.p. -1.5° to 0°C , resembling elemental bromine in appearance and possessing a vapor pressure of ~ 8 mm at 25°C (169). This nitrosyl derivative possesses a trigonal bipyramidal structure similar to the isoelectronic iron pentacarbonyl. Like iron pentacarbonyl, manganese tetracarbonyl nitrosyl is light-sensitive, being converted on exposure to light to the deep red, air-sensitive binuclear derivative $\text{Mn}_2(\text{CO})_7(\text{NO})_2$, isoelectronic with $\text{Fe}_2(\text{CO})_9$. The formation of $\text{Mn}_2(\text{CO})_{10}$ as a by-product in this irradiation reaction complicates the isolation of pure $\text{Mn}_2(\text{CO})_7(\text{NO})_2$. Other manganese nitrosyl derivatives include the carbonyl nitrosyl derivative $\text{MnCO}(\text{NO})_3$ obtained in low yield as volatile green crystals, m.p. 27°C , from the reaction between $\text{Mn}(\text{CO})_5\text{I}$ and nitric oxide (170) and the triphenylphosphine-substituted manganese nitrosyl hydride $\text{Mn}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}$ (67) obtained by reduction of the halide $\text{Mn}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Br}$ with sodium borohydride in tetrahydrofuran solution at 65°C .

Another manganese derivative is the ammonia derivative $\text{Mn}_2(\text{CO})_9\text{NH}_3$, obtained as an air-stable solid from the reaction between $\text{Na}[\text{Mn}(\text{CO})_5]$ and *O*-hydroxylaminesulfonic acid (171)

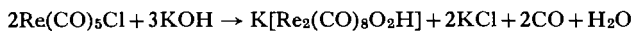


All of the chemistry of manganese, technetium, and rhenium described above involves the anions $[\text{M}(\text{CO})_5]^-$ or their substitution products. A few other anionic derivatives of these materials have also been prepared.

A binuclear derivative of interest is the anion $[\text{Mn}_2(\text{CO})_9]^{2-}$, which is isoelectronic with $\text{Fe}_2(\text{CO})_9$, and is obtained by treatment of $\text{Mn}_2(\text{CO})_{10}$ with sodium borohydride in tetrahydrofuran solution (13). Treatment of the sodium salt $\text{Na}_2[\text{Mn}_2(\text{CO})_9]$ with phosphoric acid liberates the hydride

$\text{H}_2\text{Mn}_2(\text{CO})_9$ as a red solid, which sublimes at 70–80° C in high vacuum. These compounds have not been investigated in very much detail.

A binuclear anion of rhenium $[\text{Re}_2(\text{CO})_8\text{O}_2\text{H}]^-$ has been obtained by heating $\text{Re}_2(\text{CO})_{10}$ or $\text{Re}(\text{CO})_5\text{Cl}$ with aqueous potassium hydroxide at 30–50° C or 100° C, respectively (6)



Carbonyl cyanide anions of manganese (76) and rhenium (77) have been obtained by treatment of $\text{M}(\text{CO})_5\text{Cl}$ with methanolic potassium cyanide



M = manganese or rhenium

VII

DERIVATIVES OF IRON AND RUTHENIUM

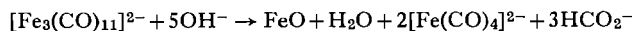
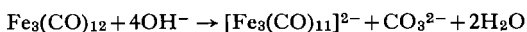
Anions of iron carbonyls form, with few exceptions, the only anionic carbonyl compounds known for this group of metals. One ruthenium carbonyl anion, $[\text{C}_5\text{H}_5\text{Ru}(\text{CO})_2]^-$, has been investigated. Osmium appears to have been completely neglected in this area of carbonyl chemistry.

A. Iron Carbonyl Anions without Other Ligands

Several anionic carbonyl derivatives of iron have been obtained by treatment of the three carbonyls of iron, $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$, with alkali metals, hydroxide ion, or nitrogen bases.

Treatment of iron pentacarbonyl with aqueous or alcoholic hydroxide ion gives air-sensitive solutions of $[\text{HFe}(\text{CO})_4]^-$ or $[\text{Fe}(\text{CO})_4]^{2-}$ (2, 7). Acidification of such solutions yields the very volatile but unstable hydride $\text{H}_2\text{Fe}(\text{CO})_4$ (172, 173). Oxidation of $[\text{HFe}(\text{CO})_4]^-$ solutions with freshly prepared manganese dioxide or nitromethane yields first in a fast reaction the dark red-orange $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion, characterized by a band in the visible spectrum at 480 $m\mu$ (7). Further oxidation with these oxidizing agents yields, in a slower reaction, the red-brown $[\text{HFe}_3(\text{CO})_{11}]^-$, characterized by a band in the visible spectrum at 540 $m\mu$ (7). The $[\text{HFe}(\text{CO})_4]^-$ anion under certain conditions appears to be oxidized slowly by water, giving the $[\text{Fe}_2(\text{CO})_8]^{2-}$ ion with evolution of hydrogen (173).

Treatment of $\text{Fe}_2(\text{CO})_9$ with aqueous hydroxide ion gives a dark red-orange solution of the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion (174). Treatment of $\text{Fe}_3(\text{CO})_{12}$ with hydroxide ion yields the $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ ion, which is degraded by excess hydroxide ion to iron(II) oxide and the mononuclear $[\text{Fe}(\text{CO})_4]^{2-}$ (174)



Under other conditions the degradation of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ by hydroxide ion is reported to proceed as far as the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion (7).

Acidification of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ is reported to give $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ as an unstable violet-red oil, readily decomposing to give $\text{Fe}_3(\text{CO})_{12}$ (174). Acidification of $[\text{Fe}_2(\text{CO})_8]^{2-}$ is reported to give $\text{Fe}_3(\text{CO})_{12}$ (173). These reactions and the oxidation reactions described above form the basis of a frequently used preparation of $\text{Fe}_3(\text{CO})_{12}$ from the commercially available $\text{Fe}(\text{CO})_5$ (175). Iron pentacarbonyl is first allowed to react with sodium hydroxide in aqueous methanol to give the $[\text{Fe}(\text{CO})_4]^{2-}$ ion. This is then oxidized with a freshly prepared suspension of manganese dioxide. After decomposing the excess manganese dioxide with a mild reducing agent, preferably iron(II) sulfate, the reaction mixture is acidified to liberate $\text{Fe}_3(\text{CO})_{12}$ in excellent yield.

In this preparation of $\text{Fe}_3(\text{CO})_{12}$ it is apparent that it is immaterial whether the $[\text{Fe}(\text{CO})_4]^{2-}$ ion is oxidized to $[\text{Fe}_3(\text{CO})_8]^{2-}$ or $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, since both of these anions form $\text{Fe}_3(\text{CO})_{12}$ on acidification, the trinuclear derivative via the unstable $\text{H}_2\text{Fe}_3(\text{CO})_{11}$. Indeed, the red fumes frequently observed during the acidification process may be due to the formation of $\text{H}_2\text{Fe}_3(\text{CO})_{11}$, although this does not appear to have been conclusively demonstrated.

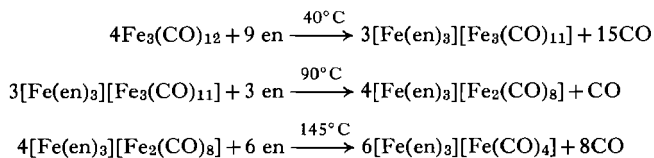
The reduction of either $\text{Fe}(\text{CO})_5$ or $\text{Fe}_3(\text{CO})_{12}$ with sodium metal in liquid ammonia (21) or of $\text{Fe}_3(\text{CO})_{12}$ with sodium dispersion or amalgam in tetrahydrofuran or other ethereal solvents (51) gives the anion $[\text{Fe}(\text{CO})_4]^{2-}$. The reduction in ethereal solvents is especially valuable in providing a facile means of obtaining $[\text{Fe}(\text{CO})_4]^{2-}$ in the absence of hydroxylic solvents or nitrogen bases, both of which interfere with reactions of $[\text{Fe}(\text{CO})_4]^{2-}$ with certain reagents, especially acid chlorides.

Reaction of various iron carbonyls with Lewis bases yields a rather bewildering variety of iron carbonyl anions depending on the base, the iron carbonyl derivative, and the reaction conditions. A comprehensive

discussion of these reactions will not be attempted in this chapter. Only the more interesting and significant aspects will be pointed out.

Treatment of iron pentacarbonyl with liquid ammonia gives $(\text{NH}_4)_2[\text{Fe}(\text{CO})_4]$ (22). Treatment of iron pentacarbonyl with aqueous ammonia in the presence of pyridine (15) or hydroxylamine (14) gives $[\text{Fe}(\text{NH}_3)_6][\text{Fe}_2(\text{CO})_8]$.

Treatment of $\text{Fe}_3(\text{CO})_{12}$ with ethylenediamine at 40°C gives the salt $[\text{Fe}(\text{en})_3][\text{Fe}_3(\text{CO})_{11}]$, which gives $[\text{Fe}(\text{en})_3][\text{Fe}_2(\text{CO})_8]$ on further heating with ethylenediamine at 90°C . The latter compound gives $[\text{Fe}(\text{en})_3][\text{Fe}(\text{CO})_4]$ on further treatment with ethylenediamine at 145°C .



Treatment of $\text{Fe}(\text{CO})_5$ with piperidine at low temperatures gives bright yellow crystals of the composition $\text{Fe}(\text{CO})_5(\text{piperidine})_3$ which are unstable above 0°C and of unknown structure (19). If the reaction between iron pentacarbonyl and piperidine is carried out in benzene at 85°C , $[\text{Fe}(\text{formyl-piperidine})_6][\text{Fe}_4(\text{CO})_{13}]$ is formed. In this case the carbon monoxide liberated from the iron pentacarbonyl carbonylates the base to form an aldehyde derivative (19). Treatment of $\text{Fe}(\text{CO})_5$ with pyrrolidine at low temperatures gives a material of composition $\text{Fe}(\text{CO})_5(\text{pyrrolidine})_2$, probably related to the $\text{Fe}(\text{CO})_5(\text{piperidine})_3$ discussed above (19).

Treatment of $\text{Fe}_3(\text{CO})_{12}$ with pyridine at room temperature or irradiation of $\text{Fe}(\text{CO})_5$ with pyridine gives $[\text{Fe}(\text{py})_6][\text{Fe}_4(\text{CO})_{13}]$, one of the most convenient preparations of the $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ ion (17). Treatment of $[\text{Fe}(\text{py})_6][\text{Fe}_4(\text{CO})_{13}]$ with ammonia causes displacement of the pyridine ligands to give $[\text{Fe}(\text{NH}_3)_6][\text{Fe}_4(\text{CO})_{13}]$ (17). Acidification of the $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ anion with hydrochloric acid gives the hydride $\text{H}_2\text{Fe}_4(\text{CO})_{13}$ as a brown-black pyrophoric solid which gives a deep red ether solution (17).

When iron pentacarbonyl and *o*-phenanthroline are heated very briefly in acetone at 65°C , the blue unstable compound $\text{Fe}(\text{CO})_5(o\text{-phen})$ of unknown structure is obtained (16). If iron pentacarbonyl or $\text{Fe}_3(\text{CO})_{12}$ are heated with *o*-phenanthroline in acetone, benzene, or pyridine for a somewhat longer time, $[\text{Fe}(o\text{-phen})_3][\text{Fe}_2(\text{CO})_8]$ is produced (16). This derivative was also prepared independently by mixing solutions of $[\text{Fe}_2(\text{CO})_8]^{2-}$ and $[\text{Fe}(o\text{-phen})_3]^{2+}$. $[\text{Fe}(o\text{-phen})_3][\text{Fe}_4(\text{CO})_{13}]$ has also been obtained (16).

The compounds now recognized as ionic derivatives, $[\text{Fe}(o\text{-phen})_3][\text{Fe}_2(\text{CO})_8]$ and $[\text{Fe}(o\text{-phen})_3][\text{Fe}_4(\text{CO})_{13}]$, were once believed to be the non-ionic derivatives $\text{Fe}_2(\text{CO})_5(o\text{-phen})_2$ and $\text{Fe}_3(\text{CO})_7(o\text{-phen})_2$, respectively (176).

Similar reactions of iron carbonyl with other pyridine derivatives, *o*-phenylenediamine, isoquinoline, pyrrolidone, and *N*-methylpyrrolidone have also been described (177).

Treatment of $\text{Fe}_3(\text{CO})_{12}$ with pyridine *N*-oxide in benzene at room temperature gives the brown pyrophoric $[\text{Fe}(\text{C}_5\text{H}_5\text{NO})_6][\text{Fe}_4(\text{CO})_{13}]$ (18). Irradiation of iron pentacarbonyl with dimethylsulfoxide in benzene solution at 80°C gives the red-black, slightly air-sensitive $[\text{Fe}(\text{Me}_2\text{SO})_6][\text{Fe}_4(\text{CO})_{13}]$ (18). Irradiation of iron pentacarbonyl with triphenylphosphine oxide or triphenylarsine oxide in benzene solution at 80°C gives dark red materials formulated as $[\text{Fe}(\phi_3\text{PO})_2][\text{Fe}_2(\text{CO})_8]$ and $[\text{Fe}(\phi_3\text{AsO})_3][\text{Fe}_2(\text{CO})_8]$, respectively (18). The apparently low coordination numbers of two or three for the cationic iron atoms in these two compounds seem peculiar.

Treatment of $\text{Fe}_3(\text{CO})_{12}$ with methanol produces derivatives of the $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ ion (not isolated in the pure state) (178) rather than compounds such as $\text{Fe}(\text{CO})_3 \cdot \text{CH}_3\text{OH}$ and $\text{Fe}(\text{CO})_3 \cdot 1/2\text{CH}_3\text{OH}$, as was once believed (179).

The iron carbonyl anions described above are air-sensitive both in solution and in the solid state. Many of the solid compounds are pyrophoric. They range in color from the colorless (when pure) $[\text{Fe}(\text{CO})_4]^{2-}$ ion to the black-brown $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ ion. They form precipitates with certain large cations, especially the cations $[\text{M}(\text{base})_6]^{2+}$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$; base = NH_3 , ethylenediamine, and especially *o*-phenanthroline). A quantitative method of analyzing solutions for these anions involves their precipitation with $[\text{Fe}(o\text{-phen})_3]^{2+}$, ignition of the precipitate to Fe_2O_3 , and weighing of the Fe_2O_3 . From a knowledge of the types of iron carbonyl anions present the amounts of cationic and anionic iron in the precipitate may then be calculated (180).

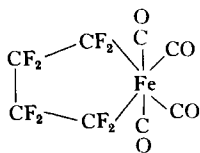
As indicated above, acidification of the anions $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, and $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ yields the unstable hydrides $\text{H}_2\text{Fe}(\text{CO})_4$, $\text{H}_2\text{Fe}_3(\text{CO})_{11}$, and $\text{H}_2\text{Fe}_4(\text{CO})_{13}$. Although $\text{H}_2\text{Fe}(\text{CO})_4$ is the least stable of these hydrides, decomposing in the pure state well below room temperature, it has been investigated in the greatest detail because of its greater availability and its greater volatility, which permits transfer as vapor diluted with carbon monoxide, in which condition it is more stable. $\text{H}_2\text{Fe}(\text{CO})_4$ has been found

to be a weak acid with $K_1 = 3.6 \times 10^{-5}$ and $K_2 = 1 \times 10^{-14}$ (98). Despite the experimental difficulties involved, the density and surface tension of $\text{H}_2\text{Fe}(\text{CO})_4$ at -70°C have been measured (181).

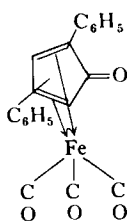
The polynuclear anions $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, and $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ react with carbon monoxide under pressure to form the mononuclear derivative $[\text{Fe}(\text{CO})_4]^{2-}$ in all cases, the required reaction temperatures being 50°C for the binuclear derivative, 100°C for the trinuclear derivative, and 200°C for the tetranuclear derivative (14).

No stable compounds of the type $\text{R}_2\text{Fe}(\text{CO})_4$ with iron-carbon σ bonds have been isolated by the reaction between $[\text{Fe}(\text{CO})_4]^{2-}$ and alkyl halides such as methyl iodide. However, the perfluoroalkyl derivatives $(\text{R}_f)_2\text{Fe}(\text{CO})_4$ ($\text{R}_f = \text{C}_2\text{F}_5$ and C_3F_7) have been obtained as air-stable very pale yellow crystals by the reaction between $\text{Na}_2[\text{Fe}(\text{CO})_4]$ prepared in *tetrahydrofuran* and the perfluoroacyl chlorides R_fCOCl . The intermediate perfluoroacyl derivatives $(\text{R}_f\text{CO})_2\text{Fe}(\text{CO})_4$ were not isolated, but instead were decarbonylated spontaneously in the boiling tetrahydrofuran (50). For reasons which are not clear at the present time the yields of the perfluoroalkyl compounds $(\text{R}_f)_2\text{Fe}(\text{CO})_4$ in this reaction were only about 15%. Attempts to prepare $(\text{CF}_3)_2\text{Fe}(\text{CO})_4$ by this technique have been unsuccessful. A related compound is the extremely stable perfluorotetramethylene derivative $\text{C}_4\text{F}_8\text{Fe}(\text{CO})_4$ (XXIX) (182) obtained from tetrafluoroethylene and iron pentacarbonyl. This fluorocarbon derivative was first erroneously formulated as a tricarbonyl derivative (183).

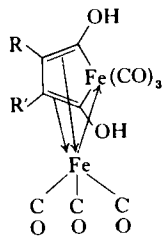
A compound believed at one time to be of the $\text{R}_2\text{Fe}(\text{CO})_4$ type is the yellow crystalline derivative originally formulated as $(\text{C}_6\text{H}_5\text{C}\equiv\text{C})_2\text{Fe}(\text{CO})_4$, yellow needles, m.p. $222-222.5^\circ\text{C}$, first obtained from phenylacetylene and iron pentacarbonyl in the presence of nickel tetracarbonyl, ethanol, water, and acetic acid (184). It is now well known, however, that this is π -diphenylcyclopentadienone-iron tricarbonyl (XXX) (185). Related compounds are now well known.



(XXIX)



(XXX)

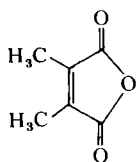


(XXXI)

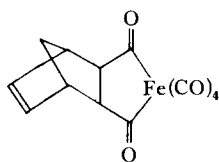
Reaction of acetylene itself with the $[\text{HFe}(\text{CO})_4]^-$ anion under pressure gives a 45% yield of a yellow solid of composition $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$, volatile at $70\text{--}80^\circ\text{C}/0.1\text{ mm}$ (186). For several years the structure of this compound was a mystery. Further work demonstrated its ability to act as a weak acid, forming the air-sensitive anion $[\text{Fe}_2\text{C}_{10}\text{H}_2\text{O}_8]^{2-}$ which reacted with dimethyl sulfate to form a dimethyl derivative (187). The parent complex $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ could also be benzoylated with benzoyl chloride in the presence of pyridine (187).

Further work on $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ has demonstrated both chemically (188) and by X-ray crystallography (189), the structure (XXXI) ($\text{R} = \text{R}' = \text{H}$) for $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_2$ and analogous structures for its derivatives. Thus $\text{Fe}_2\text{C}_{10}\text{H}_4\text{O}_8$ forms a diacetate when acetylated under mild conditions; the analogous compound prepared from propyne ($\text{R} = \text{H}$, $\text{R}' = \text{CH}_3$) forms a monoacetate when acetylated under mild conditions; and the analogous compound obtained from 2-butyne ($\text{R} = \text{R}' = \text{CH}_3$) remains unchanged when acetylated under mild conditions. All of these compounds give diacetates when acetylated under more vigorous conditions. It thus appears that the two hydroxyl groups are placed unsymmetrically with respect to the propyne molecule and that the hydroxyl substituents are sufficiently close to the acetylene residue to suffer steric hindrance from methyl substituents on the latter (188). The X-ray structure determination was carried out on the derivative obtained from 2-butyne (XXXI; $\text{R} = \text{R}' = \text{CH}_3$) and confirmed the proposed structure (189).

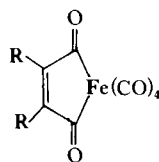
Of particular interest is the oxidation of the complexes $\text{Fe}_2\text{C}_{10}\text{H}_2\text{R}_2\text{O}_8$ (XXXI; $\text{R} = \text{R}' = \text{CH}_3$ or H) with aqueous ferric chloride to give a product of composition $(\text{RC}_2\text{R})\text{Fe}(\text{CO})_6$ (190). Oxidation of the dimethyl derivative with cold concentrated nitric acid gives dimethylmaleic anhydride (XXXII). The derivative $(\text{HC}_2\text{H})\text{Fe}(\text{CO})_6$ forms a Diels-Alder adduct (XXXIII) with cyclopentadiene; the adduct may be oxidized to succinic acid. All of these data indicate that the derivatives $(\text{RC}_2\text{R})\text{Fe}(\text{CO})_6$ are cyclic σ -bonded diacyl derivatives of the type $(\text{RCO})_2\text{Fe}(\text{CO})_4$ (XXXIV) derived from maleic acid derivatives. Four of the six carbonyl groups are metal



(XXXII)



(XXXIII)



(XXXIV)

carbonyl groups bonded to the iron atom and the remaining two carbonyl groups are acyl carbonyl groups.

As seen above, compounds of the type $R_2Fe(CO)_4$ with iron-carbon σ bonds are known only when R is a perfluoroalkyl radical or a maleoyl radical. However, compounds of this type where the iron atom is σ -bonded to an element other than carbon, are somewhat more common. Derivatives are known in which the iron atom is σ -bonded to gold, mercury, tin, and lead.

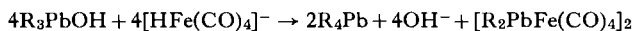
Treatment of a solution of the $[HFe(CO)_4]^-$ ion with methylmercuric hydroxide gives the yellow-white compound $(CH_3Hg)_2Fe(CO)_4$ (191). This is unstable, disproportionating on standing or on heating to $\sim 80^\circ C$ to form the insoluble, inert, stable polymeric derivative $[HgFe(CO)_4]_n$ (XXXV)



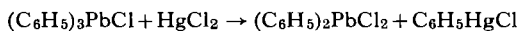
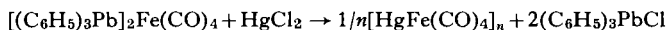
The mercury derivative $[HgFe(CO)_4]_n$ is also obtainable in a variety of other reactions, such as the treatment of $[HFe(CO)_4]^-$ with mercuric salts such as the cyanide (192), treatment of dialkylmercury derivatives with iron pentacarbonyl (193), and the disproportionation of $Hg[Fe(CO)_3NO]_2$ (80). Treatment of $(C_6H_5)_3PAuCl$ with $[Fe(CO)_4]^{2-}$ gives the stable compound $[(C_6H_5)_3PAu]_2Fe(CO)_4$ (162), which may be considered to be isoelectronic with the mercury derivative $(CH_3Hg)_2Fe(CO)_4$.

Treatment of solutions of the $[HFe(CO)_4]^-$ anion with the dialkyltin dichlorides R_2SnCl_2 ($R = CH_3$ or C_4H_9) gives the yellow derivatives $[R_2SnFe(CO)_4]_2$ (XXXVI; $E = Sn$) (194, 195). These compounds may also be obtained by heating iron pentacarbonyl in ethylcyclohexane at $\sim 135^\circ C$ with tetraalkyltin derivatives of the general formula $R_2SnR'_2$ [$R =$ alkyl group bonded to the tin atom with an sp^3 carbon atom (methyl, ethyl, butyl, etc.); $R' =$ group bonded to the tin atom with an sp^2 carbon atom (phenyl or vinyl)] (195). In this reaction the phenyl or vinyl groups are lost to give the derivatives $[R_2SnFe(CO)_4]_2$ ($R =$ methyl, ethyl, or butyl).

Treatment of the lead compounds R_3PbOH ($R =$ phenyl or cyclohexyl) with $[HFe(CO)_4]^-$ gives the yellow-orange derivatives $(R_3Pb)_2Fe(CO)_4$ ($R =$ phenyl or cyclohexyl) in $\sim 50\%$ yield (193, 196). In the case of the acyclic saturated alkyl compounds R_3PbOH ($R =$ methyl, propyl, or butyl) the brown to dark red derivatives $[R_2PbFe(CO)_4]$ (XXVI; $E = Pb$; $R =$ methyl, propyl, or butyl) are obtained, the intermediate derivatives $(R_3Pb)_2Fe(CO)_4$ being unstable with respect to $[R_2PbFe(CO)_4]_2$ and R_4Pb (196, 197)

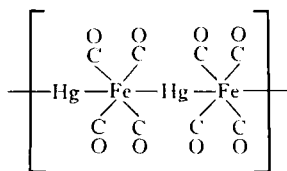


$[(\text{C}_6\text{H}_5)_3\text{Pb}]_2\text{Fe}(\text{CO})_4$ is cleaved by mercuric chloride to form $[\text{HgFe}(\text{CO})_4]_n$, $\text{C}_6\text{H}_5\text{HgCl}$, and $(\text{C}_6\text{H}_5)_2\text{PbCl}_2$ in the following sequence of reactions (198)

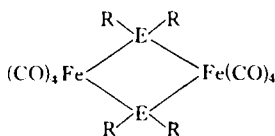


Similar attempted cleavage reactions of the lead-iron derivative with cadmium(II) iodide, copper(II) chloride dihydrate, cobalt(II) chloride hexahydrate, bismuth(III) bromide, and $\text{K}[\text{PbI}_3]$ failed to give any iron carbonyl derivatives of these metals (198). The black air-sensitive derivative of divalent lead $[\text{PbFe}(\text{CO})_4]_n$ has been obtained on treatment of $[\text{HFe}(\text{CO})_4]^-$ with basic lead(II) acetate (199).

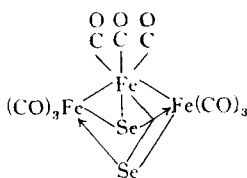
Several interesting iron carbonyl derivatives of the chalcogens have been obtained. Treatment of $[\text{Fe}(\text{CO})_4]^{2-}$ with the anions CkO_3^{2-} ($\text{Ck} = \text{S}, \text{Se}, \text{Te}$) followed by acidification at 0°C gives $\text{Fe}_3(\text{CO})_9\text{Ck}_2$ as solids ranging in color from deep red for the sulfur derivative to black-gray for the tellurium derivative (200). $\text{Fe}_3(\text{CO})_9\text{S}_2$, on attempted sublimation at $70^\circ\text{C}/0.1\text{ mm}$, undergoes extensive decomposition, only trace quantities of sublimate being obtained (201). X-ray structural determinations on $\text{Fe}_3(\text{CO})_9\text{Se}_2$ have indicated the structure (XXXVII) for this compound (202). An isomeric



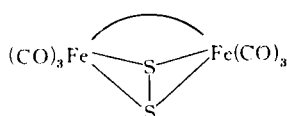
(XXXV)



(XXXVI)



(XXXVII)



(XXXVIII)

$\text{Fe}_3(\text{CO})_9\text{S}_2$, a red-violet solid readily and efficiently sublimable at $70^\circ\text{C}/0.1\text{ mm}$, has been obtained by the reaction between triiron dodecacarbonyl and episulfide derivatives (201), but the structure of this derivative has not been

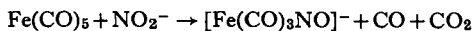
determined. Treatment of $[\text{Fe}(\text{CO})_4]^{2-}$ with polysulfide ion (e.g., S_5^{2-}), followed by acidification, yields a mixture of the $\text{Fe}_3(\text{CO})_9\text{S}_2$ obtained from sulfite ion and the ruby red derivative $\text{Fe}_2(\text{CO})_6\text{S}_2$, m.p. 46.5°C , readily sublimable in vacuum (200). X-ray structural studies on $\text{Fe}_2(\text{CO})_6\text{S}_2$ have indicated the structure (XXXVIII) with a sulfur-sulfur bond (202). The preparation of $\text{Fe}_2(\text{CO})_6\text{S}_2$ from sulfoxylic acid and $[\text{Fe}(\text{CO})_4]^{2-}$ has been briefly mentioned (203).

A variety of very perplexing derivatives of metalloids have been obtained by treatment of $[\text{Fe}(\text{CO})_4]^{2-}$ with an appropriate derivative of the metalloid in aqueous solution followed by acidification (204). Thus, treatment of $[\text{Fe}(\text{CO})_4]^{2-}$ with arsenite ion followed by acidification gives black air-sensitive $\text{As}_2\text{Fe}_3(\text{CO})_{11}$, which is soluble in organic solvents. Similar treatment of $[\text{Fe}(\text{CO})_4]^{2-}$ with antimony(III) oxide gives a dark red derivative of stoichiometry $\text{SbFe}(\text{CO})_4$. If a mixture of antimony(III) and antimony(V) is introduced into the reaction with $[\text{Fe}(\text{CO})_4]^{2-}$, black air-sensitive needles of $\text{SbFe}_2(\text{CO})_8$ are obtained. Similar treatment of $[\text{Fe}(\text{CO})_4]^{2-}$ with either a bismuth(III) derivative or "sodium bismuthate" gives a black material of composition $\text{Bi}_2\text{Fe}_5(\text{CO})_{20}$. Some of the more metallic elements also give such derivatives. Thus $[\text{Fe}(\text{CO})_4]^{2-}$ reacts with ammonium hexachlorostannate(IV) to give dark red $\text{Sn}_2\text{Fe}_5(\text{CO})_{20}$ after acidification. A similar reaction with the acetates of lead(II) or lead(IV) gives black $\text{PbFe}_3(\text{CO})_{12}$. The relationship between this derivative and the black compound $[\text{PbFe}(\text{CO})_4]_n$ (199) is not clear. Finally $[\text{Fe}(\text{CO})_4]^{2-}$ reacts similarly with thallium(III) oxide or thallium(I) carbonate to give the dark orange, very air-sensitive $\text{Tl}_2\text{Fe}_3(\text{CO})_{12}$ (204). The structures of none of these compounds are understood. They may be related, however, to the iron carbonyl carbide $\text{Fe}_5(\text{CO})_{15}\text{C}$, formed in very low yield as a by-product in the reaction of $\text{Fe}_3(\text{CO})_{12}$ with certain acetylenes. The structure of this compound was recently elucidated by X-ray methods (205).

B. The $[\text{Fe}(\text{CO})_3\text{NO}]^-$ Anion and Nitrogen Derivatives of Iron Carbonyl Produced From Related Systems

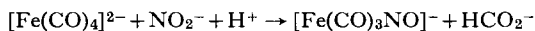
The deep yellow $[\text{Fe}(\text{CO})_3\text{NO}]^-$ anion has been obtained by the following methods:

(1) *Treatment of iron pentacarbonyl with nitrite ion at $25-40^\circ\text{C}$ in methanol solution (81)*



More recently it has been found that addition of sodium methoxide to the reaction mixture in this preparation greatly improves the yield (80). This method is the most convenient and useful preparation of the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ ion.

(2) *Refluxing solutions of $[\text{Fe}(\text{CO})_4]^{2-}$ and nitrite ion* for several hours in a mole ratio of 1:1.5 (8, 82):



Intermediates in this reaction appear to be the polynuclear anions $[\text{HFe}_2(\text{CO})_8]^-$ and $[\text{HFe}_3(\text{CO})_{11}]^-$ (82).

(3) *Treatment of $[\text{HFe}(\text{CO})_4]^-$ with hydroxylamine* (82). This reaction gives an $\sim 30\%$ yield of $[\text{Fe}(\text{CO})_3\text{NO}]^-$, significant by-products being the imide $[\text{Fe}(\text{CO})_3\text{NH}]_2$ (XXXIX) ($\sim 10\%$ yield) and Fe_2O_3 , formed by the hydroxylamine's action as an oxidizing agent. Although hydroxylamine is normally considered as a reducing agent, its oxidizing power under certain conditions is hardly surprising since it is formally a "half-amide" of hydrogen peroxide (82).

(4) *Treatment of $\text{Fe}(\text{CO})_2(\text{NO})_2$ either with sodium amalgam in tetrahydrofuran or with potassium hydroxide* (8). In any of the preparations of $[\text{Fe}(\text{CO})_3\text{NO}]^-$ from $\text{Fe}(\text{CO})_2(\text{NO})_2$, it is impossible for more than two-thirds of the iron to be converted to the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ anion due to the fact that a species with three carbon monoxides per iron atom is being formed from a species with only two carbon monoxides per iron atom without the addition of carbon monoxide. This theoretical limitation on the yield as well as the necessity for preparing and handling the unstable $\text{Fe}(\text{CO})_2(\text{NO})_2$ make this one of the least desirable methods for preparing $[\text{Fe}(\text{CO})_3\text{NO}]^-$.

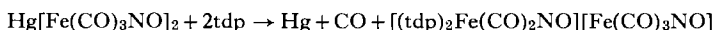
Salts of the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ ion are yellow and air-sensitive. Treatment of aqueous solutions of this ion with $[\text{Fe}(o\text{-phen})_3]^{2+}$, $[\text{Ni}(o\text{-phen})_3]^{2+}$, or $[(\text{C}_5\text{H}_5)_2\text{Co}]^+$ gives water-insoluble precipitates of the corresponding $[\text{Fe}(\text{CO})_3\text{NO}]^-$ salts of these cations (8). Treatment of a methanol solution of the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ anion with ammonium hexachlorostannate(IV) gives the red covalent tin(IV) derivative $\text{Sn}[\text{Fe}(\text{CO})_3\text{NO}]_4$, which sublimes at 120°C in high vacuum with partial decomposition (80). If the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ solution is treated with a hydrochloric acid solution of divalent or tetravalent tin, the red derivative $\text{ClSn}[\text{Fe}(\text{CO})_3\text{NO}]_3$ is obtained. This derivative cannot be sublimed in high vacuum without decomposition (80). Treatment of a solid salt of the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ ion with hydrogen chloride in

dimethyl ether gives the extremely unstable hydride $\text{HFe}(\text{CO})_3\text{NO}$, which decomposes above -45°C , sometimes explosively (80).

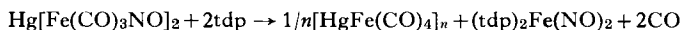
Of particular interest is the mercury derivative $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$, readily obtainable from solutions of the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ ion and mercury(II) cyanide as a red solid, and insoluble in water but soluble in organic solvents. This mercury derivative is thermally unstable, decomposing slowly even at room temperature to give $[\text{HgFe}(\text{CO})_4]_n$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ (80)



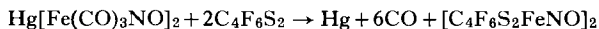
This reaction provides a convenient source for small quantities of $\text{Fe}(\text{CO})_2(\text{NO})_2$. On reaction with triphenylphosphine in benzene at room temperature $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$ forms the orange-yellow insoluble substitution product $\text{Hg}[\text{Fe}(\text{CO})_2(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]_2$ (206). Treatment of $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$ with tris(dimethylamino)phosphine in refluxing benzene for ~ 6 hours gives the ionic derivative $[(\text{tdp})_2\text{Fe}(\text{CO})_2\text{NO}][\text{Fe}(\text{CO})_3\text{NO}]$ (206)



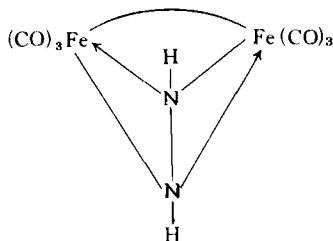
If the reaction conditions are more vigorous, the major product is the dark red, volatile compound $(\text{tdp})_2\text{Fe}(\text{NO})_2$, a derivative of $\text{Fe}(\text{CO})_2(\text{NO})_2$ (206)



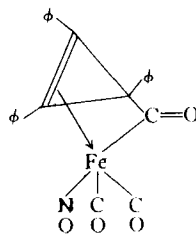
Reaction of $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$ with bis(trifluoromethyl)dithietene in refluxing benzene gives a black volatile compound (206):



Reaction between the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ anion and triphenylcyclopropenyl bromide in methanol solution gives a 14% yield of the maroon crystalline derivative π -triphenylcyclopropenecarbonyliron dicarbonyl nitrosyl (XL), in which the double bond of a cyclopropene system is π -bonded to the iron atom (207)



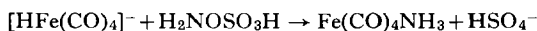
(XXXIX)



(XL)

An iron carbonyl derivative also formed in the reaction of $[\text{HFe}(\text{CO})_4]^-$ with certain nitrogen compounds is the orange, fairly air-stable, very volatile imine $[\text{Fe}(\text{CO})_3\text{NH}]_2$, for which is suggested structure (XXXIX), with a nitrogen–nitrogen bond analogous to the sulfur–sulfur bond recently demonstrated for the similar $\text{Fe}_2(\text{CO})_6\text{S}_2$ (202). For example, treatment of $[\text{HFe}(\text{CO})_4]^-$ with nitrite ion in a mole ratio of 1 to 0.5 for several hours at temperatures not exceeding 40°C gives a 2.3% yield of $[\text{Fe}(\text{CO})_3\text{NH}]_2$ (171, 203). Somewhat better results are obtained in the reaction between $[\text{HFe}(\text{CO})_4]^-$ and hydroxylamine, the yield rising to 9.7% (82, 171). $[\text{Fe}(\text{CO})_3\text{NH}]_2$ is decomposed by hydrogen chloride (171). It is inert to benzoylation with benzoyl chloride and to methylation with diazomethane (171). On treatment with excess nitric oxide in boiling benzene the deep black, nonvolatile $[\text{Fe}(\text{NO})_2\text{NH}]_2$ is obtained (171), which is much less soluble than $[\text{Fe}(\text{CO})_3\text{NH}]_2$.

Treatment of $[\text{HFe}(\text{CO})_4]^-$ with *O*-hydroxylaminesulfonic acid at -5°C gives a 62% yield of the bright yellow, partially water-soluble, pyrophoric amine derivative $\text{Fe}(\text{CO})_4\text{NH}_3$ (171)



This decomposes slowly above 0°C to give an ionic derivative



C. Cyclopentadienyl Metal Carbonyl Anions of Iron and Ruthenium

Among the most stable and most readily prepared series of compounds with transition metal–carbon σ bonds are the iron derivatives $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$, many of which are readily obtainable from the sodium salt $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ and an appropriate organic halide (52). This sodium salt may be conveniently prepared by allowing the dimeric cyclopentadienyliron dicarbonyl $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ to react with excess dilute sodium amalgam in tetrahydrofuran (52) or methanol (51). Tetrahydrofuran is the preferred solvent for many reactions of $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ with organic halides, especially acid chlorides which react with methanol. The dimeric cyclopentadienyliron dicarbonyl $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ is in turn extremely easily and inexpensively obtained in 70% or higher yield by boiling a mixture of the very inexpensive iron pentacarbonyl and dicyclopentadiene for several hours under nitrogen (208). This ready availability of the $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$

derivatives, permitting relatively large-scale reactions, has recently prompted extensive investigations in several laboratories engaged in organometallic chemistry of transition metals.

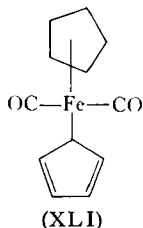
The analogous ruthenium derivatives have been much less investigated, only a single paper (53) having appeared discussing these compounds. The cyclopentadienylruthenium dicarbonyl dimer $[\text{C}_5\text{H}_5\text{Ru}(\text{CO})_2]_2$, obtainable from $[\text{Ru}(\text{CO})_2\text{I}_2]_n$ and sodium cyclopentadienide (209), besides involving the much rarer element ruthenium, does not appear to be as easily prepared in quantity as its iron analog.

Treatment of $\text{Na}[\text{M}(\text{CO})_2\text{C}_5\text{H}_5]$ ($\text{M} = \text{Fe}$ or Ru) with methyl or ethyl iodides gives, in good yield, the solid methyl derivatives $\text{CH}_3\text{M}(\text{CO})_2\text{C}_5\text{H}_5$ ($\text{M} = \text{Fe}$ or Ru) or the liquid ethyl derivatives $\text{C}_2\text{H}_5\text{M}(\text{CO})_2\text{C}_5\text{H}_5$ ($\text{M} = \text{Fe}$ or Ru), respectively (52, 53). The phenyl derivative $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ may be similarly obtained from iodobenzene and $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$, but due to the inertness of iodobenzene the yield is 5% or less (52). Reaction of perfluoroallyl chloride with $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ yields the perfluoropropenyl compound $\text{CF}_3\text{CF}=\text{CFe}(\text{CO})_2\text{C}_5\text{H}_5$ rather than the corresponding perfluoroallyl derivative (50). Compounds containing two iron atoms have been obtained by treating the halides $\text{Br}(\text{CH}_2)_n\text{Br}$ ($n = 3, 4, 5$, or 6) with $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ (103).

Similar compounds of the type $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$ have also been obtained by treatment of the halides $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ with Grignard reagents or sodium cyclopentadienide (52). The Grignard reagents used include the methyl-, ethyl-, and phenylmagnesium halides. However, the syntheses involving these Grignard reagents are inferior to the corresponding syntheses of the same compounds from the sodium salt $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ and the corresponding iodide because of a greater tendency for the occurrence of side reactions such as those producing $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. The reaction between $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ and sodium cyclopentadienide, however, yields a compound, $(\sigma\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (XLI), not obtainable from $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$, which contains both a σ -bonded and a π -bonded cyclopentadienyl group (52).

A few acyl derivatives have been synthesized by treatment of $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ with certain acid chlorides (102, 211). $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ with acetyl chloride gives the acetyl derivative $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ (102, 211). The trifluoroacetyl derivative $\text{CF}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ (117) may be obtained by treatment of $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ with trifluoroacetic anhydride, but appreciable quantities of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ are also produced in this reaction.

Acyl derivatives containing two iron atoms may be obtained by allowing $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ to react with the difunctional acid chlorides $\text{ClCO}(\text{CH}_2)_n\text{COCl}$ ($n = 3$ or 4) (211). In addition, reaction between $\text{Cl}(\text{CH}_2)_3\text{COCl}$ and $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ yields $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CH}_2)_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ which contains one $-\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ σ -bonded to an alkyl carbon atom and one $-\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ group σ -bonded to an acyl carbon atom (211). Another derivative containing two iron atoms is $\text{C}_3\text{N}_3\text{Cl}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$, obtained from $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ and cyanuric chloride (103). Attempts to decarbonylate any of these acyl derivatives to the corresponding alkyl derivatives by heating under conditions suitable for the decarbonylation of the corresponding acylmanganese pentacarbonyl derivatives have always been unsuccessful (102, 211). However, the methyl derivative $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ may be carbonylated at 125°C and 130 atm pressure to give the acetyl compound $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ (102).



These alkyl and acyl derivatives of the general formula $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$ are yellow to orange liquids or solids of varying air-sensitivity, melting generally below 150°C (Table II). The compounds containing one iron atom are readily sublimed in high vacuum. Even some of the compounds containing two iron atoms, such as $(\text{CH}_2)_3[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ (103), may also be sublimed in high vacuum, but with greater difficulty. These iron compounds are insoluble in and stable to water, but soluble in organic solvents, the mononuclear derivatives being more soluble than the binuclear derivatives. The ruthenium derivatives, as far as they are known, possess properties similar to the iron derivatives except that they are colorless rather than yellow or orange (54).

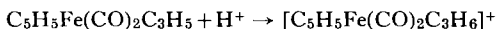
A rather unusual series of related compounds are the dialkylcarbamyl derivatives $\text{R}_2\text{NCOFe}(\text{CO})_2\text{C}_5\text{H}_5$ ($\text{R} = \text{methyl or ethyl}$) obtained from $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ and the corresponding dialkylcarbamyl chlorides (211). These orange, rather unstable compounds are decomposed by water to form weakly alkaline solutions containing the amine R_2NH . Unless purified by sublimation these compounds decompose rapidly on storage.

The hydrides corresponding to these alkyl derivatives, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ (68) and $\text{C}_5\text{H}_5\text{Ru}(\text{CO})_2\text{H}$ (53), are yellow and colorless liquids respectively, and are very air-sensitive. They have not been obtained by acidification of the sodium salts $\text{Na}[\text{M}(\text{CO})_2\text{C}_5\text{H}_5]$ ($\text{M} = \text{Fe}$ or Ru) but instead by reduction of the halides $\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{X}$ with sodium borohydride in tetrahydrofuran. They decompose rapidly at room temperature to form $[\text{C}_5\text{H}_5\text{M}(\text{CO})_2]_2$ and hydrogen. The hydride $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ also appears to be an unstable intermediate in the sodium borohydride reduction of the $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]^+$ cation (212).

Some interesting allylic and olefinic cyclopentadienyliron dicarbonyl derivatives have been prepared (216, 217, 218, 219). Treatment of $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ with allyl chloride gives the air-sensitive yellow liquid σ -allyl derivative $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_3\text{H}_5$ (XLII) (101). On heating, this compound, unlike σ -allylmanganese pentacarbonyl (99, 100), is not converted into a π -allyl derivative. Instead the allyl group is lost, resulting in formation of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. However, irradiation of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_3\text{H}_5$ (XLII) produces the yellow crystalline air-sensitive π -allyl derivative $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{C}_3\text{H}_5$ (XLIII) with loss of one mole of carbon monoxide (101). This π -allyl derivative is rather unstable thermally, reportedly decomposing at $\sim 65^\circ\text{C}$. (101).

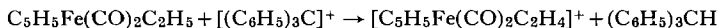
The olefinic derivatives $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{RCH}=\text{CH}_2)]\text{X}$ ($\text{X} = \text{PF}_6^-$, etc.) (XLIV) have been obtained by the following methods:

(1) *Protonation of σ -allyl derivatives.* Treatment of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_3\text{H}_5$ (XLII) with strong acid gives salts of the π -propene cation $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_3\text{H}_6]^+$ (XLIV; $\text{R} = \text{CH}_3$) (101, 213)

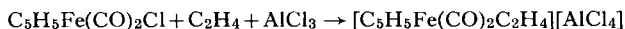


Protonation of $(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5))$ (XLI) with hydrogen chloride in petroleum ether gives the cation $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_6)]^+$ (XLV), isolable as the hexafluorophosphate (215). Hydrogenation of this cation gives $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and treatment with triphenylphosphine at 85° displaces the π -bonded cyclopentadiene residue to form the cation $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3]^+$, previously prepared by a different route (212).

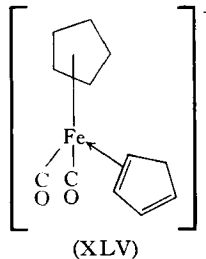
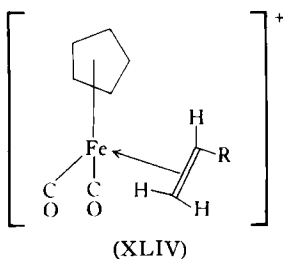
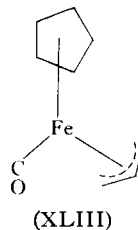
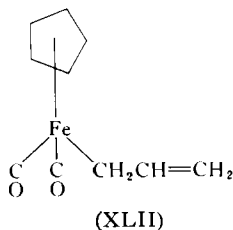
(2) *Hydride abstraction from σ -alkyl derivatives with β -hydrogen atoms.* Treatment of the ethyl derivative $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_2\text{H}_5$ with triphenylmethyl carbonium ion gives salts of the π -ethylene cation $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_2\text{H}_4]^+$ (XLIV; $\text{R} = \text{H}$) (214)



(3) *Reaction of the halides $C_5H_5Fe(CO)_2X$ with olefins in the presence of a Lewis acid.* Treatment of $C_5H_5Fe(CO)_2Cl$ with ethylene under pressure in the presence of aluminum chloride gives the cation $[C_5H_5Fe(CO)_2C_2H_4]^+$ (XLIV; $R = H$) (216)

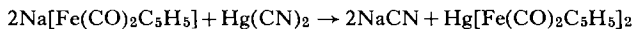


When this reaction is carried out with diolefins, only one of the double bonds reacts and becomes π -bonded to the iron atom (217). These olefinic

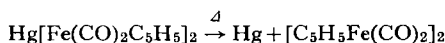


cationic complexes of iron are quite stable, forming yellow solutions which give stable yellow precipitates with hexafluorophosphate ion or similar large anions.

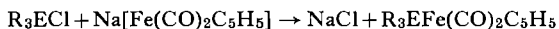
Several compounds in which an $-Fe(CO)_2C_5H_5$ group is σ -bonded to an element other than carbon have been prepared. Excluding the halides and other compounds not involved in the chemistry of anionic metal carbonyls, the first such derivative to be obtained was the orange crystalline mercury compound $Hg[Fe(CO)_2C_5H_5]_2$, best obtained from $Na[Fe(CO)_2C_5H_5]$ and mercury(II) cyanide (51)



More recently $Hg[Fe(CO)_2C_5H_5]_2$ has been isolated as a by-product in certain reactions involving $Na[Fe(CO)_2C_5H_5]$ prepared from sodium amalgam (35, 36, 101). $Hg[Fe(CO)_2C_5H_5]_2$ is reported to decompose on heating to $80-90^\circ C$ to form mercury and $[C_5H_5Fe(CO)_2]_2$ (51)



Several compounds containing iron σ -bonded to silicon (218), germanium, (158) and tin (157) have been prepared by the following general reaction :



E = silicon, R = methyl (218); E = germanium, R = phenyl (158); E = tin, R = phenyl (157)

These derivatives are orange solids, volatile in many cases and increasing in stability in the series Fe-Si < Fe-Ge < Fe-Sn. The iron-tin bond is so stable in $\text{R}_3\text{SnFe}(\text{CO})_2\text{C}_5\text{H}_5$ that the carbon-tin bond rather than the iron-tin bond is cleaved by halogens or hydrogen halides, forming compounds such as $\text{Cl}_3\text{SnFe}(\text{CO})_2\text{C}_5\text{H}_5$ (157).

VIII

DERIVATIVES OF COBALT

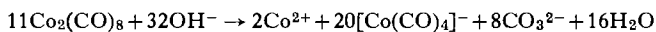
Cobalt is the only metal in this group whose anionic carbonyl compounds have been investigated in any detail. A carbonyl hydride of rhodium, presumably $\text{HRh}(\text{CO})_4$, is formed in low yield as extremely unstable pale yellow crystals by the treatment of rhodium chloride with carbon monoxide in the presence of water and a metal as reducing agent (219). However, this carbonyl hydride of rhodium has not been characterized. Therefore all of the chemistry to be discussed in this section will be cobalt chemistry.

In contrast to the several anionic carbonyl derivatives of iron, only one anionic cobalt carbonyl is known which does not contain other ligands. This is the tetrahedral $[\text{Co}(\text{CO})_4]^-$ anion, isoelectronic with the neutral $\text{Ni}(\text{CO})_4$ and with the $[\text{Fe}(\text{CO})_4]^{2-}$ anion. The $[\text{Co}(\text{CO})_4]^-$ ion may be obtained by a variety of methods such as the following :

(1) *Reduction of aqueous solutions of cobalt(II) salts in the presence of carbon monoxide.* Reduction of aqueous ammoniacal cobalt(II) solutions in the presence of carbon monoxide at atmospheric pressure with such reducing agents as sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) (220) or formamidinesulfonic acid (XLVI) (221) (obtained by hydrogen peroxide oxidation of thiourea) gives aqueous solutions of the $[\text{Co}(\text{CO})_4]^-$ ion. This method has the advantages that no cobalt carbonyl derivatives are required for starting materials and that the use of carbon monoxide under pressure is not required. The main disadvantage is that the $[\text{Co}(\text{CO})_4]^-$ ion is obtained in aqueous solution and contaminated with other materials such as ammonia and the oxidation product of the reducing agent. These materials may interfere with certain sub-

sequent reactions of the $[\text{Co}(\text{CO})_4]^-$ ion. Nevertheless, $[\text{Co}(\text{CO})_4]^-$ prepared by this method is suitable for the preparation of the heavy metal derivatives $\text{AgCo}(\text{CO})_4$ and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ (220).

(2) *Reaction of dicobalt octacarbonyl with hydroxide ion.* Dicobalt octacarbonyl reacts with aqueous or alcoholic hydroxide ion to give cobalt(II) and the $[\text{Co}(\text{CO})_4]^-$ ion, apparently according to the following equation (9)



The presence of excess hydroxide ion and the hydroxylic solvent interfere with many possible preparative uses. In addition a minimum of $\sim 9\%$ of the cobalt is converted to cobalt(II).

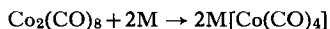
(3) *Reaction of dicobalt octacarbonyl with Lewis bases.* A very common type of reaction, discussed in detail earlier in this chapter, is the reaction of dicobalt octacarbonyl with a great variety of Lewis bases (23, 24, 54) to give the derivatives $[\text{Co}(\text{base})_6][\text{Co}(\text{CO})_4]_2$



The bases which undergo this reaction (discussed in detail in an earlier portion of this chapter) include a variety of amines, ethers, and alcohols. In general pure products were not isolated from the reactions involving oxygen bases (24). Some surprisingly weak bases, including tetrahydrofuran and acetonitrile, which are often considered as "inert" solvents, will bring about this reaction. Solutions of $[\text{Co}(\text{CO})_4]^-$ prepared by treatment of dicobalt octacarbonyl with ethanol (222) or tetrahydrofuran (223) have been used as intermediates in the preparation of the $\text{RCCo}_3(\text{CO})_9$ derivatives (to be discussed below in greater detail). Related reactions of Lewis bases with dicobalt octacarbonyl are the reactions with tricovalent phosphorus derivatives and with isocyanides to give $[(\text{R}_3\text{P})_2\text{Co}(\text{CO})_3][\text{Co}(\text{CO})_4]$ (27, 28, 29) and $[\text{Co}(\text{CNR})_5][\text{Co}(\text{CO})_4]$ (30, 31) respectively. Both of these compounds contain cations with pentavalent cobalt in the +1 oxidation state, iso-electronic with the pentavalent iron atom in the 0 oxidation state in iron pentacarbonyl. All of these reactions between dicobalt octacarbonyl and Lewis bases suffer from the disadvantage that some of the cobalt is converted to cobalt(II) or cobalt(I) rather than to $[\text{Co}(\text{CO})_4]^-$.

(4) *Reduction of dicobalt octacarbonyl with alkali metals.* Dicobalt octacarbonyl is readily reduced to the $[\text{Co}(\text{CO})_4]^-$ anion by lithium metal in

tetrahydrofuran (38) or by sodium amalgam in benzene (54), diethyl ether (55), or dimethyl ether (55)



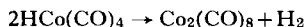
An intermediate in the reduction with sodium amalgam appears to be the mercury derivative $\text{Hg}[\text{Co}(\text{CO})_4]_2$. This method of preparation of $[\text{Co}(\text{CO})_4]^-$ possesses the advantage, at least theoretically, that all of the cobalt of dicobalt octacarbonyl may be converted to the $[\text{Co}(\text{CO})_4]^-$ anion.

A particularly important derivative of the $[\text{Co}(\text{CO})_4]^-$ anion is the hydrogen derivative, $\text{HCo}(\text{CO})_4$. Although this compound is commonly called cobalt carbonyl "hydride", the term "hydride" is actually a misnomer since the hydrogen atom in $\text{HCo}(\text{CO})_4$ is not hydridic but strongly protonic in character; $\text{HCo}(\text{CO})_4$ is as strong an acid as sulfuric acid (98). Because of its unusual properties and relative simplicity, $\text{HCo}(\text{CO})_4$ has been the subject of several spectroscopic (225, 228, 229) and theoretical (230) investigations.

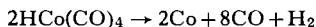
Treatment of solutions of $[\text{Co}(\text{CO})_4]^-$ with strong acids results in the formation of $\text{HCo}(\text{CO})_4$. In a convenient preparation of $\text{HCo}(\text{CO})_4$ in quantity dicobalt octacarbonyl is first treated with pyridine to give $[\text{Co}(\text{py})_6][\text{Co}(\text{CO})_4]_2$, which is then treated with sulfuric acid to give $\text{HCo}(\text{CO})_4$ in 95% yield (after allowing for the cobalt expected to be converted to the $[\text{Co}(\text{py})_6]^{2+}$ cation (23)). The deuterium analog can be obtained by substituting D_2SO_4 for the H_2SO_4 . An alternative preparation of $\text{HCo}(\text{CO})_4$ involves the reaction of dicobalt octacarbonyl with hydrogen at elevated temperatures under sufficient carbon monoxide pressure to prevent the dicobalt octacarbonyl from losing carbon monoxide to form either tetracobalt dodecacarbonyl or metallic cobalt (224). Because of the thermal instability of $\text{HCo}(\text{CO})_4$ in the absence of carbon monoxide and hydrogen pressure, the autoclave in which this reaction has been carried out must be cooled well below room temperature ($\sim -50^\circ\text{C}$) before the gases are vented. Since dicobalt octacarbonyl may be prepared by treatment of "simple" cobalt salts such as the oxide (225) or carbonate (226) with carbon monoxide and hydrogen under pressure, a direct preparation of $\text{HCo}(\text{CO})_4$ from readily available cobalt oxide or carbonate should be possible by heating with a mixture of carbon monoxide and hydrogen under pressure and then cooling the autoclave to low temperature.

$\text{HCo}(\text{CO})_4$ is a toxic, malodorous, unstable gas. It is unstable at room temperature unless handled under a stream of carbon monoxide. Its mode of decomposition appears to be dependent on its surroundings (227). In a

container with moist glass walls $\text{HCo}(\text{CO})_4$ gives dicobalt octacarbonyl and hydrogen on decomposition



However, on lightly greased surfaces $\text{HCo}(\text{CO})_4$ decomposes more completely, producing cobalt metal, carbon monoxide, and hydrogen



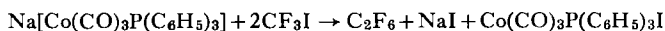
Pentacoordinate $\text{HCo}(\text{CO})_4$ is a less stable species than the tetracoordinate $[\text{Co}(\text{CO})_4]^-$, an important factor undoubtedly being the negative charge on the cobalt atom in $[\text{Co}(\text{CO})_4]^-$, which increases the strength of the cobalt–carbon monoxide bonds in the anion. For this reason it is not at all surprising that $\text{HCo}(\text{CO})_4$ is much less stable in hexane solution, where it is present as the undissociated $\text{HCo}(\text{CO})_4$, than in aqueous solution, where it is essentially completely ionized into H^+ and $[\text{Co}(\text{CO})_4]^-$ (23).

Some cobalt carbonyl anions substituted with triphenylphosphine and triphenylphosphite have been obtained. Treatment of dicobalt octacarbonyl with R_3P (R = phenyl or phenoxy) gives the substitution products $[\text{Co}(\text{CO})_3\text{PR}_3]_2$ (28). Treatment of these derivatives with dilute sodium amalgam in tetrahydrofuran gives the sodium salts $\text{Na}[\text{Co}(\text{CO})_3\text{PR}_3]$ (R = phenyl or phenoxy), which are isolable as tetrahydrofuran solvates (56, 57). Treatment of aqueous solutions of the $[\text{Co}(\text{CO})_3\text{PR}_3]^-$ anions with the $[\text{Ni}(\text{o-phen})_3]^{2+}$ cation precipitates the corresponding $[\text{Ni}(\text{o-phen})_3][\text{Co}(\text{CO})_3\text{PR}_3]_2$ salts (56, 57). Treatment of aqueous solutions of the $[\text{Co}(\text{CO})_3\text{PR}_3]^-$ anions with mercury(II) sulfate precipitates the covalent mercury derivatives $\text{Hg}[\text{Co}(\text{CO})_3\text{PR}_3]_2$ (57), also obtainable by treatment of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with the corresponding R_3P derivatives (26). An attempt to prepare the sodium salt $\text{Na}[\text{Co}(\text{CO})_3\text{As}(\text{C}_6\text{H}_5)_3]$ by reduction of $[\text{Co}(\text{CO})_3\text{As}(\text{C}_6\text{H}_5)_3]_2$ (28) with sodium amalgam in tetrahydrofuran resulted instead in the formation of $\text{Na}[\text{Co}(\text{CO})_4]$, $[\text{Co}(\text{tetrahydrofuran})_6][\text{Co}(\text{CO})_4]$, and triphenylarsine in a complex reaction (57).

The corresponding hydrides $\text{HCo}(\text{CO})_3\text{PR}_3$ (R = phenyl or phenoxy) may be obtained by acidification of the corresponding sodium salts with hydrochloric or phosphoric acid (56, 57). The compounds $\text{HCo}(\text{CO})_3\text{L}$ decrease in acidity and increase in stability in the order $\text{L} = \text{CO}$ ($\text{dec} > -20^\circ\text{C}$, $K = 1$); $\text{L} = \text{P}(\text{OC}_6\text{H}_5)_3$ ($\text{dec} > 0^\circ\text{C}$, $K = 1.13 \times 10^{-5}$); and $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ ($\text{dec} > +20^\circ\text{C}$, $K = 1.09 \times 10^{-7}$). These data, as well as the similar data on vanadium carbonyl hydride derivatives discussed above,

suggest that the most acidic hydrides are the least stable to thermal decomposition. The data on the cobalt compound suggest in addition that ligands which are particularly efficient in removing electron density from the metal atom by partial metal-ligand double-bonding (such as carbon monoxide) decrease the thermal stability and increase the acidity of hydride derivatives. Substituting some of the carbon monoxide ligands with ligands which are less efficient in removing electron density from the metal atom by partial metal-ligand double-bonding (such as triphenylphosphine) increases the thermal stability and decreases the acidity of hydride derivatives. The hydride $\text{HCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ gives precipitates with heavy metal ions such as Ag^+ , Tl^+ , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+} , which are presumably covalent derivatives similar to those formed from the $[\text{Co}(\text{CO})_4]^-$ anion discussed below (56).

Treatment of the sodium salt $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with compounds which are sources of positive halogens gives the carbonyl halides $\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3\text{X}$ (156). Thus $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with trifluoromethyl iodide gives the red-brown light- and air-sensitive carbonyl iodide derivative $\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3\text{I}$, which crystallizes with two molecules of benzene



Similar treatment of $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with *N*-bromosuccinimide at -80°C gives the similar light- and air-sensitive bromide $\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3\text{Br}$. This bromide on treatment with phenyllithium gives a 5 to 10% yield of the bright yellow, relatively air-stable phenyl derivative $\text{C}_6\text{H}_5\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ (156).

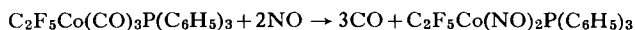
Some alkylcobalt tetracarbonyl derivatives of general formula $\text{RCo}(\text{CO})_4$ have been obtained. These pentacoordinate derivatives are much less stable than the corresponding hexacoordinate alkylmanganese pentacarbonyl derivatives $\text{RMn}(\text{CO})_5$. Treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with a deficiency of methyl iodide under carefully controlled conditions gives a 2 to 4% yield of the very unstable $\text{CH}_3\text{Co}(\text{CO})_4$, a volatile material which decomposes above -35°C (55). Similar unstable ethyl and benzyl $\text{RCo}(\text{CO})_4$ derivatives have been obtained by treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with $[(\text{C}_2\text{H}_5)_3\text{O}][\text{BF}_4]$ and benzyl bromide, respectively (231).

The perfluoroalkylcobalt tetracarbonyl compounds $\text{R}_f\text{Co}(\text{CO})_4$ are considerably more stable than the very unstable hydrogen analogs mentioned above. Thus, treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with trifluoroacetic anhydride gives the yellow liquid trifluoroacetyl derivative $\text{CF}_3\text{COC}(\text{CO})_4$, m.p. 4°C (111).

On heating to temperatures above 55° C this trifluoroacetyl derivative undergoes decarbonylation to produce the yellow liquid trifluoromethyl derivative $\text{CF}_3\text{Co}(\text{CO})_4$ (111), also obtainable in a single step from $\text{Li}[\text{Co}(\text{CO})_4]$ and trifluoroacetyl chloride (38), the intermediate trifluoroacetyl derivative being decarbonylated without isolation. In contrast to the very unstable methyl derivative $\text{CH}_3\text{Co}(\text{CO})_4$, discussed above, $\text{CF}_3\text{Co}(\text{CO})_4$ possesses noteworthy stability and can be distilled at $\sim 90^\circ \text{C}$ at atmospheric pressure without decomposition. Similar unusually stable derivatives of the C_2F_5 (38, 112), C_3F_7 (38, 112), and C_7F_{15} (112) groups have been obtained. A related fluorocarbon derivative of cobalt is $(\text{CO})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$ (232), obtained by treatment of dicobalt octacarbonyl with tetrafluoroethylene.

A variety of triphenylphosphine derivatives of alkyl, perfluoroalkyl, and acyl cobalt carbonyls of general formula $\text{RCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ have been prepared. The $\text{RCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ derivatives appear to be more stable than the corresponding unsubstituted $\text{RCo}(\text{CO})_4$ derivatives. Thus, treatment of $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with methyl iodide gives the yellow methyl derivative $\text{CH}_3\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$, which decomposes at $+20^\circ \text{C}$, in contrast to $\text{CH}_3\text{Co}(\text{CO})_4$ which decomposes at -35°C (56, 57). Of intermediate stability is the similarly prepared dirty yellow triphenyl phosphite derivative $\text{CH}_3\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3$, which decomposes at $\sim 0^\circ \text{C}$ (56, 57).

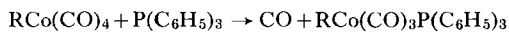
Similar fluorocarbon derivatives have also been prepared. Treatment of $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with the perfluoro acid anhydrides $(\text{R}_f\text{CO})_2\text{O}$ [$\text{R}_f = \text{CF}_3$ (111) or C_2F_5 (112)], gives the yellow perfluoroacyl derivatives $\text{R}_f\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$. On heating the trifluoroacetyl derivative to 130°C (111) or the pentafluoropropionyl derivative (112) to 75°C decarbonylation occurs to produce the corresponding colorless or pale yellow compounds $\text{R}_f\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$. $\text{C}_2\text{F}_5\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ on treatment with excess nitric oxide at $60\text{--}70^\circ \text{C}$ gives the dinitrosyl derivative $\text{C}_2\text{F}_5\text{Co}(\text{NO})_2\text{P}(\text{C}_6\text{H}_5)_3$ as a dark violet-brown solid, m.p. 65°C (112)



All of the $\text{RCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ derivatives described above were obtained by reaction of the sodium salt $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with an appropriate organic halide or fluorinated acid anhydride. Some $\text{RCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ compounds have also been obtained by treatment of $\text{RCo}(\text{CO})_4$ with triphenylphosphine. In many cases the intermediate $\text{RCo}(\text{CO})_4$ because of its instability, is not isolated. Instead $\text{Na}[\text{Co}(\text{CO})_4]$ is treated with the appropriate halide and triphenylphosphine then added. Alternatively, a mixture

of $\text{Na}[\text{Co}(\text{CO})_4]$ and triphenylphosphine (which do *not* react to form $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$) may be treated with the desired halide. In either case the reaction may be one of the two following types, differing as to whether the molecule of carbon monoxide displaced by the triphenylphosphine is expelled as free carbon monoxide or converted into an acyl carbonyl group:

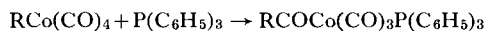
(1) *Expulsion of carbon monoxide:*



$\text{R} = \text{C}_2\text{F}_5$ (112), CH_3CO (233, 234), $\text{C}_2\text{H}_5\text{CO}$ (233, 234), $(\text{CH}_3)_2\text{CHCO}$ (233, 234), $\text{CH}_3(\text{CH}_2)_4\text{CO}$ (234), $\text{C}_6\text{H}_5\text{CO}$ (234), *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CO}$ (234), terephthalyl (234), CF_3CO (234), $\text{CH}_3\text{OCH}_2\text{CO}$ (234), $\text{C}_2\text{H}_5\text{OCOCH}_2\text{CO}$ (234), $\text{CH}_3\text{OCO}(\text{CH}_2)_2\text{CO}$, (234), ClCH_2CO (234), $\text{Cl}(\text{CH}_2)_3\text{CO}$ (234), NCCH_2 (234)

Similarly $\text{C}_2\text{F}_5\text{Co}(\text{CO})_4$ reacts with triphenylarsine or triphenylstibine to form $\text{C}_2\text{F}_5\text{Co}(\text{CO})_3\text{Pn}(\text{C}_6\text{H}_5)_3$ [$\text{Pn} = \text{As}$ or Sb (112)]. The acyl derivatives $\text{R}'\text{COCO}(\text{CO})_4$ required for many of these preparations may be obtained *in situ* either from $\text{Na}[\text{Co}(\text{CO})_4]$ and the corresponding acyl halide $\text{R}'\text{COX}$ or from $\text{Na}[\text{Co}(\text{CO})_4]$, the alkyl halide $\text{R}'\text{X}$, and carbon monoxide, carbonylation of the intermediate alkyl derivative $\text{R}'\text{Co}(\text{CO})_4$ occurring (234).

(2) *Conversion of a metal carbonyl group into an acyl carbonyl group.*

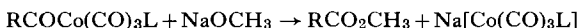


$\text{R} = \text{CH}_3$ (233) or $\text{CH}_3(\text{CH}_2)_4$ (235)

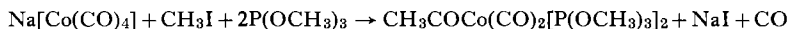
The $\text{CH}_3\text{Co}(\text{CO})_4$ required for this reaction was obtained *in situ* from $\text{Na}[\text{Co}(\text{CO})_4]$ and methyl iodide and the $\text{CH}_3(\text{CH}_2)_4\text{Co}(\text{CO})_4$ by the addition of $\text{HCo}(\text{CO})_4$ to 1-pentene. In the latter reaction some of the isomeric $\text{CH}_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{Co}(\text{CO})_4$ is formed, which also forms the corresponding acyl triphenylphosphine derivative on treatment with triphenylphosphine.

The factor which determines whether the carbon monoxide displaced by the triphenylphosphine is expelled as free carbon monoxide or is converted into an acyl carbonyl group appears to be the electronegativity of the group to which the cobalt tetracarbonyl residue is bonded. Very electronegative groups such as the perfluoroalkyl, acyl, and cyanomethyl groups favor expulsion of the carbon monoxide. Ordinary alkyl groups without electronegative substituents, such as the methyl and *n*-amyl groups, favor conversion into an acyl carbonyl group. This factor of electronegativity is the same factor that was observed above to determine the relative ease of carbonylation of $\text{RMn}(\text{CO})_5$ derivatives.

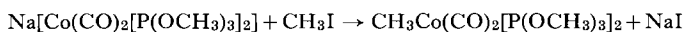
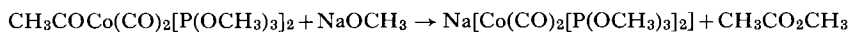
Some interesting syntheses (236) have been carried out utilizing alternately the reactions of alkylcobalt carbonyl derivatives with tricovalent phosphorus derivatives and the cleavage of acylcobalt carbonyl derivatives to the corresponding anions with methanolic sodium methoxide, e.g.



Treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with methyl iodide and trimethylphosphite gives the cobalt dicarbonyl $\text{CH}_3\text{COC}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2$



Cleavage of this acetyl derivative with methanolic sodium methoxide followed by alkylation of the resulting sodium salt with methyl iodide gives the methyl derivative $\text{CH}_3\text{Co}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2$

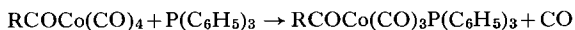


This methyl derivative may then be heated with some more trimethylphosphite in pentane at 75°C to give the acetyl derivative $\text{CH}_3\text{COC}(\text{CO})[\text{P}(\text{OCH}_3)_3]_3$, one of the two terminal carbonyl groups becoming an acyl carbonyl group



A similar series of transformations has been carried out using trimethylolpropane phosphite (designated as TMPP) (XLVI). One of the intermediates in the sequence of reactions with TMPP, $\text{CH}_3\text{COC}(\text{CO})_2(\text{TMPP})_2$, undergoes hydrogenolysis to form the hydride $\text{HCo}(\text{CO})_2(\text{TMPP})_2$ when treated in tetrahydrofuran solution with 200 atm of hydrogen at 60°C (236). This hydride possesses unusual stability, melting at $155\text{--}160^\circ\text{C}$ with decomposition. It is thus much more stable than even $\text{HCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$.

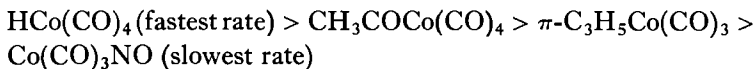
Some kinetic studies involving the reactions of various cobalt carbonyl derivatives with triphenylphosphine have recently been reported. The rate constants were measured for the reactions of a variety of acylcobalt tetracarbonyl derivatives with triphenylphosphine according to the following equation (237)



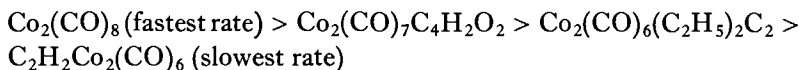
The reaction was found to be first order with respect to the acylcobalt tetracarbonyl derivative. The rate of the reaction was increased by an increase in the size of the acyl group and decreased by an increase in the electron-withdrawing tendencies of the acyl group.

In a further study the reaction rates of a variety of cobalt carbonyl derivatives of different types with triphenylphosphine were measured (238). The following series of reactivity were observed:

(1) *Mononuclear Derivatives*

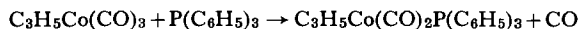


(2) *Binuclear Derivatives*



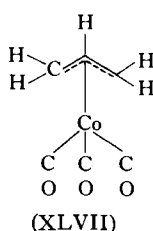
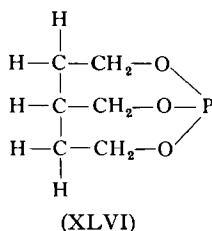
A cobalt carbonyl derivative of particular interest is π -allylcobalt tricarbonyl (XLVII), a red-yellow, air-sensitive volatile liquid readily obtained from $\text{Na}[\text{Co}(\text{CO})_4]$ and allyl halides (100, 210, 239). Substituted π -allylcobalt tricarbonyl derivatives may likewise be obtained by reaction between substituted allyl halides and $\text{Na}[\text{Co}(\text{CO})_4]$ (100, 210). Of particular significance is $\text{C}_4\text{H}_7\text{Co}(\text{CO})_3$, obtained from 1-bromo-2-butene and $\text{Na}[\text{Co}(\text{CO})_4]$. Previously a rather puzzling compound of this composition had been obtained by generating $\text{HCo}(\text{CO})_4$ from $[\text{Co}(\text{CO})_4]^-$ and acetic acid in the presence of butadiene (240). This compound remained poorly understood until the discovery of π -allylcobalt tricarbonyl and the subsequent demonstration of identity of the $\text{C}_4\text{H}_7\text{Co}(\text{CO})_3$ obtained from 1-bromo-2-butene and $\text{Na}[\text{Co}(\text{CO})_4]$ and the $\text{C}_4\text{H}_7\text{Co}(\text{CO})_3$ obtained from $\text{HCo}(\text{CO})_4$ and butadiene (210). This clearly shows $\text{C}_4\text{H}_7\text{Co}(\text{CO})_3$ to be a methyl-substituted π -allyl derivative. Further confirmation was obtained by the detection of two isomeric $\text{C}_4\text{H}_7\text{Co}(\text{CO})_3$ compounds, apparently differing as to whether the methyl group attached to the π -allyl system is pointed toward (XLVIII) or away from (XLIX) the cobalt atom (241).

π -Allylcobalt tricarbonyl reacts with triphenylphosphine to give the yellow crystalline dicarbonyl $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$ with loss of one mole of carbon monoxide (233, 239)



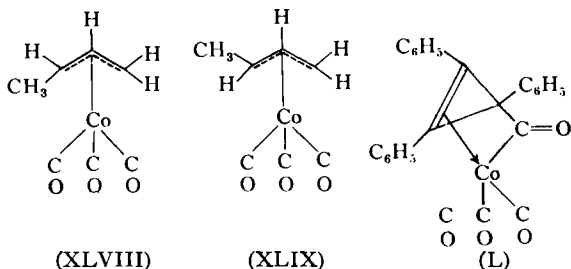
Kinetic studies have been carried out on the reactions of a variety of substituted π -allylcobalt tricarbonyl derivatives with triphenylphosphine (242). The rates of these reactions were found to be independent of phosphine concentration above ~ 0.06 M. Substituting the hydrogen atom on the center carbon atom of the three carbon atoms of the π -allyl system with either

larger electron-supplying or electron-withdrawing groups increased the rate of reaction. Thus, the effect of the substituent on the center carbon atom on the reaction with triphenylphosphine appears to be steric rather than electronic.



Some acrylylcobalt carbonyl derivatives have been investigated. Treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with acrylyl chloride appears to give an unstable acrylylcobalt tricarbonyl derivative which could not be isolated in the pure state but which was identified from its infrared spectrum (239). If this acrylylcobalt carbonyl complex is treated *in situ* with triphenylphosphine, evolution of one mole of carbon monoxide occurs and the complex $\text{CH}_2=\text{CHCOCo}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$ is obtained as a moderately stable yellow solid (242). Similar complexes were observed in the reactions of the crude acrylylcobaltcarbonyl complex with triphenylarsine, tri-*p*-anisylphosphine, tributylphosphine, and trimethyl phosphite, but these were not isolated in the pure state (239). Treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with acrylyl chloride under much more vigorous conditions gives a low yield of a purple compound $\text{CH}_2=\text{CHCCo}_3(\text{CO})_9$ (117) related to compounds discussed below.

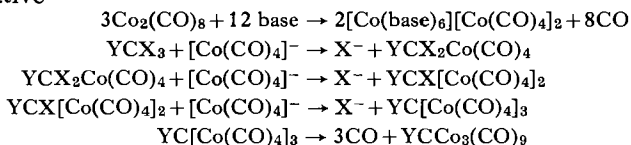
Reaction of $\text{Na}[\text{Co}(\text{CO})_4]$ with the triphenylcyclopropenyl cation in acetonitrile gives π -triphenylcyclopropenylcarbonylcobalt tricarbonyl (L) as air-stable yellow crystals, m.p. $134\text{--}135.5^\circ\text{C}$ (207).



An interesting series of cobalt carbonyl derivatives are the deep violet trinuclear derivatives of general formula $\text{YCCo}_3(\text{CO})_9$. These were first prepared by treatment of the acetylene complexes $\text{Co}_2(\text{CO})_6(\text{RC}_2\text{H})$ with

a strong mineral acid such as hydrochloric or sulfuric acid, to give the derivatives $\text{RC}_2\text{H}_2\text{Co}_3(\text{CO})_9$ (243). An erroneous NMR spectrum misled original structural investigations. Later the derivative $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{Co}_3(\text{CO})_9$ was prepared and degraded with bromine to the previously unknown tribromide $\text{C}_6\text{H}_5\text{CH}_2\text{CBr}_3$ in 35% yield (244). The tribromide degradation product was identified by usual organic chemistry techniques. The complex $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{Co}_3(\text{CO})_9$ was also oxidized by hydrogen peroxide to phenylacetic acid. These data indicate structure (I.I) for the complex $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{Co}_3(\text{CO})_9$.

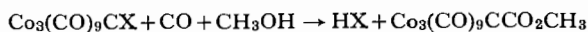
The synthesis of $\text{YCCo}_3(\text{CO})_9$ derivatives by strong acid treatment of the acetylene complexes $\text{Co}_2(\text{CO})_6(\text{RC}_2\text{H})$ not only is limited to acetylenes with a hydrogen atom bonded to at least one of the two carbon atoms of the triple bond but also is limited to the preparation of complexes of this type of the general formula $\text{RCH}_2\text{CCo}_3(\text{CO})_9$. A much more general synthesis of $\text{YCCo}_3(\text{CO})_9$, suitable at least in theory for almost any Y group, was discovered, apparently independently by three groups of workers, one in England (222), one in Hungary (223), and one in Italy (245). In this synthesis $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$ is treated with trihalomethane derivatives of the type CX_3Y [X = halogen, Y = methyl (222), chlorine (222, 223, 245), fluorine (222, 245), phenyl (222, 223), $\text{CO}_2\text{C}_2\text{H}_5$ (222, 245), CO_2H (222), $\text{CH}(\text{OCOCH}_3)_2$ (222), trifluoromethyl (222), bromine (245), iodine (245), and hydrogen (223, 245)]. In general the reaction is carried out at the boiling point of a weakly basic solvent such as tetrahydrofuran or ethanol. This reaction probably proceeds by attack of the basic solvent on the dicobalt octacarbonyl to form the $[\text{Co}(\text{CO})_4]^-$ anion. Three moles of this anion could then condense stepwise to form an unstable derivative $\text{YC}[\text{Co}(\text{CO})_4]_3$ which would then lose one mole of carbon monoxide for each cobalt atom and form the necessary cobalt-cobalt bonds, resulting then in the $\text{YCCo}_3(\text{CO})_9$ derivative



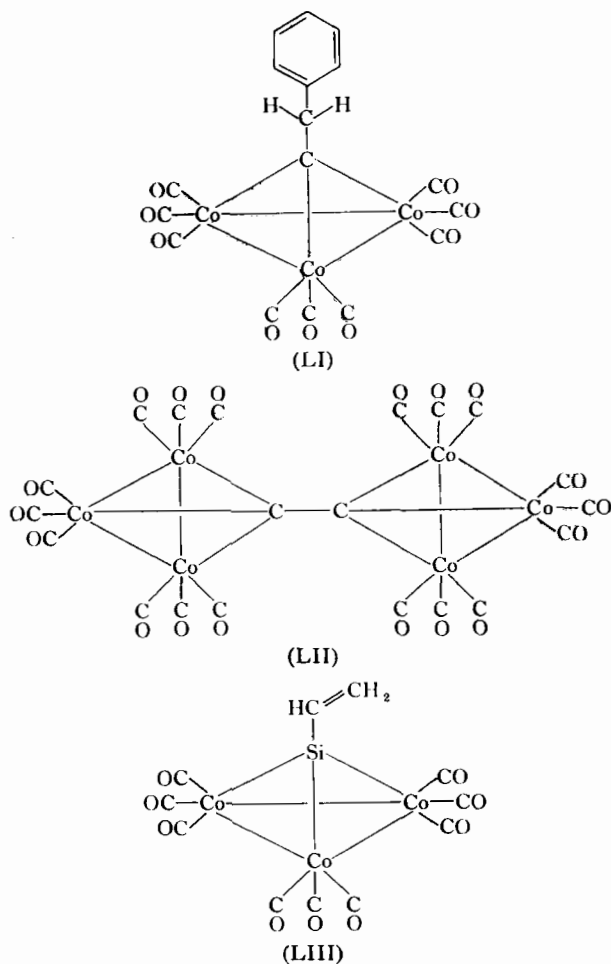
The significance of the $[\text{Co}(\text{CO})_4]^-$ ion in this synthesis of $\text{YCCo}_3(\text{CO})_9$ derivatives is supported by the preparation of $\text{CH}_3\text{CCo}_3(\text{CO})_9$ from $\text{Na}[\text{Co}(\text{CO})_4]$ and CH_3CCl_3 in refluxing tetrahydrofuran (117).

Several side reactions of interest are observed in the preparation of various $\text{YCCo}_3(\text{CO})_9$ derivatives by this general synthetic method. In the

preparation of $\text{Co}_3(\text{CO})_9\text{CCl}$ by refluxing dicobalt octacarbonyl with carbon tetrachloride in methanol solution appreciable quantities of the methyl ester $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{CH}_3$ are formed as a by-product (223). The same ester is obtained by heating $\text{Co}_3(\text{CO})_9\text{CBr}$ with methanol to 55°C (245). Apparently some of the carbon monoxide, either liberated in the original reaction of the CX_4 derivative with the dicobalt octacarbonyl or in the decomposition of some of the $\text{Co}_3(\text{CO})_9\text{CX}$ derivative, can carbonylate the cobalt complex to produce an ester, according to the following equation



The analogous ethyl ester can be formed similarly in ethanol (245).



Another interesting $\text{YCCo}_3(\text{CO})_9$ derivative is $[\text{Co}_3(\text{CO})_9\text{C}]_2$ (LII), obtained in $\sim 1\%$ yield by treatment of $[\text{Co}(\text{CO})_4]^-$ with hexachloroethane (223). It is also a minor by-product ($\sim 1\%$ yield) in the reaction of $[\text{Co}(\text{CO})_4]^-$ with carbon tetrachloride (223).

The compounds $\text{YCCo}_3(\text{CO})_9$ form purple crystalline derivatives soluble in organic solvents, but insoluble in water. Despite the presence of three cobalt atoms all of the compounds except for $[\text{Co}_3(\text{CO})_9\text{C}]_2$ may be sublimed readily in vacuum, and some of them are reported to distill with steam without decomposition (222). They appear to be some of the most air-stable cobalt carbonyl derivatives.

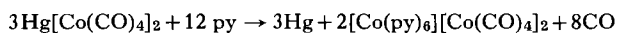
A silicon analog $\text{CH}_2=\text{CHSiCo}_3(\text{CO})_9$ (LIII) has been reported as a purple-black crystalline solid formed by refluxing dicobalt octacarbonyl and tetravinylsilane in petroleum ether (246).

A variety of cobalt carbonyl derivatives have been obtained in which the cobalt atom is σ -bonded to an element other than carbon. These have been obtained both by "wet" methods involving metathesis of a solution of $[\text{Co}(\text{CO})_4]^-$ with an appropriate derivative of the element to be bonded to cobalt and by "dry" methods involving high-pressure reactions of carbon monoxide with a mixture of cobalt metal or one of its compounds and an appropriate derivative of the other element. Thus, treatment of aqueous solutions of $[\text{Co}(\text{CO})_4]^-$ with silver nitrate or mercury(II) cyanide gave the derivatives $\text{AgCo}(\text{CO})_4$ or $\text{Hg}[\text{Co}(\text{CO})_4]$, respectively (220). The mercury derivative can also be prepared by the "dry" method, involving treatment of a mixture of mercury(II) bromide and cobalt metal with 200 atm of carbon monoxide at 150°C (247). The silver derivative $\text{AgCo}(\text{CO})_4$ could not be prepared by the "dry" method (247). The yellow zinc and cadmium derivatives $\text{M}[\text{Co}(\text{CO})_4]_2$ ($\text{M} = \text{Zn}$ or Cd) can be obtained by treatment of cobalt(II) bromide, cobalt metal, or dicobalt octacarbonyl with zinc or cadmium metal in the presence of carbon monoxide under pressure (247).

Heating a mixture of indium and cobalt metals with carbon monoxide under pressure gives the red indium derivative $\text{In}[\text{Co}(\text{CO})_4]_3$. Treatment of thallium metal with cobalt metal or cobalt(II) bromide gives either the yellow air-sensitive sublimable thallium(I) derivative $\text{TlCo}(\text{CO})_4$ or the dark violet sublimable thallium(III) derivative $\text{Tl}[\text{Co}(\text{CO})_4]_3$, depending on the reaction conditions (247). Treatment of a mixture of metallic tin and cobalt(II) bromide with carbon monoxide under pressure gives the tin(II) derivative $\text{Sn}[\text{Co}(\text{CO})_4]_2$ (247). The metals germanium, gold, antimony, lithium, beryllium, magnesium, and calcium failed to give cobalt carbonyl

derivatives when mixed with various cobalt derivatives and treated with carbon monoxide under pressure (247). A stable triphenylphosphine-gold complex $(\text{C}_6\text{H}_5)_3\text{PAuCo}(\text{CO})_4$ has, however, been obtained relatively recently by the "wet" method, involving treatment of $(\text{C}_6\text{H}_5)_3\text{PAuCl}$ with $\text{Na}[\text{Co}(\text{CO})_4]$ (162). In an attempt to make a lead derivative of cobalt carbonyl, a mixture of lead metal and cobalt(II) bromide was heated with carbon monoxide under pressure, but a pure product could not be obtained (247). However, much more recently a lead acetate derivative of cobalt carbonyl $\text{CH}_3\text{CO}_2\text{PbCo}(\text{CO})_4$ was obtained as a yellow, very air-sensitive solid by treatment of basic lead(II) acetate with $\text{Na}[\text{Co}(\text{CO})_4]$ (199).

The mercury compound $\text{Hg}[\text{Co}(\text{CO})_4]_2$ appears to be the most stable of these metal cobalt tetracarbonyl derivatives, especially with respect to air oxidation. It reacts with the phosphines R_3P (R = phenyl, cyclohexyl, or ethyl) at room temperature to form the yellow, sparingly soluble solids $\text{Hg}[\text{Co}(\text{CO})_3\text{PR}_3]_2$ (26). The phenyl derivative may also be obtained from $\text{Na}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ and an appropriate mercury derivative. Treatment of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with pyridine liberates free mercury to form the salt $[\text{Co}(\text{py})_6][\text{Co}(\text{CO})_4]_2$ (26)



This reaction, preceded by the formation of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ from sodium amalgam and dicobalt octacarbonyl in a hydrocarbon solvent, is the basis of a recently proposed method for the purification of mercury (37). However, the cost of dicobalt octacarbonyl makes the widespread application of this mercury purification method unlikely. Treatment of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with trimethylphosphite also liberates mercury, producing the nonionic derivative $[\text{Co}(\text{CO})_3\text{P}(\text{OCH}_3)_3]_2$ rather than a salt (26)



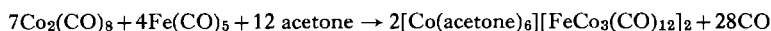
The cadmium, zinc, and tin derivatives $\text{M}[\text{Co}(\text{CO})_4]_2$ also react with triphenylphosphine to form $\text{M}[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$. However, treatment of $\text{AgCo}(\text{CO})_4$ with triphenylphosphine liberates elemental silver to form $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$ (26).

Some similar organotin derivatives of cobalt carbonyl have been prepared. Treatment of $\text{Na}[\text{Co}(\text{CO})_4]$ with tri-*n*-butyltin chloride in methanolic solution gives the yellow-brown liquid $(\text{C}_4\text{H}_9)_3\text{SnCo}(\text{CO})_4$ which loses one mole of carbon monoxide on treatment with triphenylphosphine to give the crystalline $(\text{C}_4\text{H}_9)_3\text{SnCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ (194). Similarly, treatment of the dialkyltin dihalides R_2SnCl_2 (R = methyl or *n*-butyl) with $\text{Na}[\text{Co}(\text{CO})_4]$ gives the

yellow-brown derivatives $R_2Sn[Co(CO)_4]_2$ [R = methyl (solid); R = *n*-butyl (liquid)], which likewise react with triphenylphosphine, losing one mole of carbon monoxide for each cobalt atom, to form $R_2Sn[Co(CO)_3P(C_6H_5)_3]_2$.

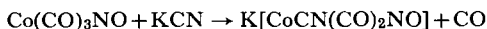
In all of the compounds described above a cobalt tetracarbonyl residue is bonded to a *non-transition* element such as tin, mercury, or most of their neighbors in the Periodic Table. A cobalt tetracarbonyl residue can also be σ -bonded to another *transition* metal provided that the transition metal also has ligands with a strong partial double-bonding ability, such as carbon monoxide or π -cyclopentadienyl, bonded to it. Two such compounds are now known (248). Of particular interest is the orange-red, very volatile ($30^\circ C/0.3$ mm), crystalline (m.p. $45-46^\circ C$) $(CO)_5Mn-Co(CO)_4$ (LIV), an unusual "pure" metal carbonyl derivative containing two different transition metals and isoelectronic with $Fe_2(CO)_9$. Unlike $Fe_2(CO)_9$, the manganese-cobalt derivative $MnCo(CO)_9$ contains only terminal carbonyl groups, as demonstrated by its infrared spectrum. Similar treatment of $Na[Co(CO)_4]$ with $C_5H_5Fe(CO)_2I$ gives the very dark red compound $(CO)_4Co-Fe(CO)_2C_5H_5$ (LV), m.p. $52-53^\circ C$, which sublimes at $36^\circ C/0.2$ mm. Like the carbonyls $Co_2(CO)_8$ and $[C_5H_5Fe(CO)_2]_2$, the mixed derivative $(CO)_4Co-Fe(CO)_2C_5H_5$ contains bridging carbonyl groups.

Heating a mixture of dicobalt octacarbonyl and iron pentacarbonyl in acetone for several hours results in the more complex iron-cobalt carbonyl derivative $[Co(acetone)_6][FeCo_3(CO)_{12}]$ (32)

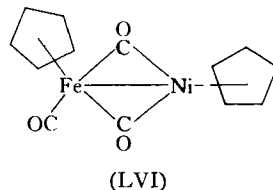
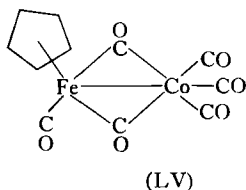
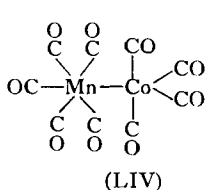


Treatment of this hexaacetonecobalt(II) derivative with potassium acetate results in the potassium salt $K[FeCo_3(CO)_{12}]$, isolated as a sesquisolvate with acetone. Aqueous solutions of $[FeCo_3(CO)_{12}]^-$ give a precipitate of $[(C_2H_5)_4N][FeCo_3(CO)_{12}]$ when treated with the tetramethylammonium ion. Treatment of $[Co(acetone)_6][FeCo_3(CO)_{12}]_2$ with hydrochloric acid gives the black crystalline hydride $HFeCo_3(CO)_{12}$, which sublimes slowly at $50-60^\circ C/0.1-0.2$ mm and is significantly soluble in hydrocarbon solvents. This $[FeCo_3(CO)_{12}]^-$ ion may be considered to be isoelectronic with the neutral $Co_4(CO)_{12}$ and presumably has a similar structure.

Some mixed cobalt carbonyl nitrosyl cyanide anions have been prepared (78). Treatment of $Co(CO)_3NO$ with potassium cyanide causes the displacement of one mole of carbon monoxide, forming the brown-red, air-sensitive potassium salt $K[CoCN(CO)_2NO]$



This anion disproportionates in neutral aqueous solution to form the dianion $[\text{CoCO}(\text{CN})_2\text{NO}]^{2-}$ and $\text{Co}(\text{CO})_3\text{NO}$

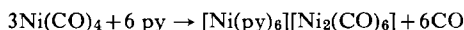


IX

DERIVATIVES OF NICKEL

Anionic metal carbonyls of palladium and platinum containing two or more carbonyl groups and analogous to those of other metals discussed in this chapter are completely unknown. The recent discovery of $[\text{C}_5\text{H}_5\text{PtCO}]_2$ (249) may ultimately create possibilities for the preparation of the $[\text{C}_5\text{H}_5\text{PtCO}]^-$ anion and $\text{C}_5\text{H}_5\text{PtCOR}$ derivatives. Even the anionic metal carbonyl chemistry of nickel is rather meager and poorly understood, despite the ready availability of nickel tetracarbonyl.

Treatment of nickel tetracarbonyl with a mixture of pyridine and hydroxide ion at 40°C for 2 hr results in the formation of a derivative of the yellow $[\text{Ni}_2(\text{CO})_6]^{2-}$ ion



A species formerly known as $\text{Ni}(o\text{-phen})(\text{CO})_2$ and assumed to be a substitution product of nickel tetracarbonyl is now believed to be the salt $[\text{Ni}(o\text{-phen})_3][\text{Ni}_2(\text{CO})_6]$ (33). Reduction of nickel tetracarbonyl with sodium or other very active metals in liquid ammonia is believed first to produce the $[\text{Ni}_2(\text{CO})_6]^{2-}$ ion, which is reported to react with liquid ammonia to form a red unstable ammoniate of the hydride $\text{H}_2\text{Ni}_2(\text{CO})_6$ (58, 59).

This $[\text{Ni}_2(\text{CO})_6]^{2-}$ anion may be precipitated in basic solution by such large cations as $[\text{M}(o\text{-phen})_3]^{2+}$ (33). However, if aqueous solutions of $[\text{Ni}_2(\text{CO})_6]^{2-}$ are acidified with weak acid the tetranuclear anion $[\text{HNi}_4(\text{CO})_9]^-$ is said to be formed (33). This is also reported to form precipitates with the tetraethylammonium cation and the $[\text{M}(o\text{-phen})_3]^{2+}$ cations ($\text{M} = \text{Fe}$ or Ni). The $[\text{Ni}_4(\text{CO})_9]^{2-}$ anion is also formed by treatment of nickel tetracarbonyl with a mixture of ethylenediamine and pyridine or, as a

red-orange solution, by reduction of nickel tetracarbonyl with sodium amalgam in tetrahydrofuran.

The evidence for the formulations of these nickel carbonyl anions is based almost entirely on elemental analyses of products. Spectroscopic data on these derivatives appear to be very meager, possibly due to the apparent instability of these compounds.

Some attempts to prepare the cyclopentadienylnickel carbonyl anion $[\text{C}_5\text{H}_5\text{NiCO}]^-$ have been made (86). Treatment of nickel tetracarbonyl with sodium cyclopentadienide was found to give a red water-soluble solution but a pure derivative of the $[\text{C}_5\text{H}_5\text{NiCO}]^-$ anion could not be isolated from this solution (86). Attempts to reduce $[\text{C}_5\text{H}_5\text{NiCO}]_2$ with sodium amalgam in methanol to give $[\text{C}_5\text{H}_5\text{NiCO}]^-$ have been unsuccessful, the major product of this reaction being the trinuclear derivative $(\text{C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ (86). A paper presented at the Organometallic Symposium in 1962 contained a brief mention of the stable red perfluoroalkyl derivatives $\text{R}_f\text{NiCOC}_5\text{H}_5$ (60) best obtained from perfluoroalkyl iodides and $[\text{C}_5\text{H}_5\text{NiCO}]_2$. The non-fluorinated methyl derivative $\text{CH}_3\text{NiCOC}_5\text{H}_5$ was reported to be very unstable (60). A detailed description of this chemistry, including the preparation of $[\text{C}_5\text{H}_5\text{NiCO}]^-$, appeared only after completion of this paper (251).

In connection with the chemistry of $-\text{NiCOC}_5\text{H}_5$ residues σ -bonded to other elements, it is of interest that biscyclopentadienylnickel and iron pentacarbonyl react in benzene at 80°C to give the dark brown $\text{C}_5\text{H}_5\text{Ni}(\text{CO})-\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (XVI) (250). The presence of bridging carbonyl groups is demonstrated by the infrared spectrum. This iron-nickel derivative is much more air-sensitive than either $[\text{C}_5\text{H}_5\text{NiCO}]_2$ or $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$.

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Heterocyclic Organoboranes

R. KÖSTER

Max-Planck Institut für Kohlenforschung,
Mülheim/Ruhr,
West Germany

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I

INTRODUCTION

In recent years, the rapid development of organoboron chemistry, through the discovery of new and improved synthetic methods, has led to extensive investigation into heterocyclic organoboranes containing ring systems of carbon and boron only. These compounds (1) strongly resemble the well-known, simple trialkylboranes (2), and the properties of both will be discussed.

Up to the present, only saturated aliphatic compounds with one boron atom have been well studied. Unsaturated aliphatic ring systems (3, 41, 42) and compounds of two or more boron atoms (4a, b) are still only slightly understood.

Our knowledge of the synthesis and structure of heterocyclic organoboranes became possible not only through simplified preparations of these materials, but also through the use of modern analytic techniques. Vapor phase chromatography has been used to separate mixtures formed in organoborane syntheses (5, 6, 22) while mass spectroscopy (7), infrared Raman and NMR spectroscopic studies have markedly aided characterization.

This article will discuss the alkyl exchange and thermal isomerization reactions of organoboranes; and various syntheses, properties, and reactions of heterocyclic organoboranes with one boron atom; and will present a summary of heterocyclic organoboranes with two or more boron atoms.

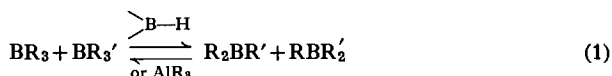
II

GENERAL REACTIONS OF ORGANOBORANES

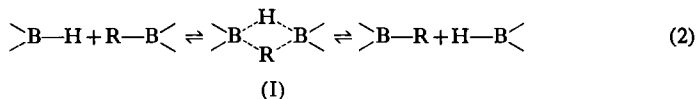
A. Alkyl Exchange Reactions

Alkyl and aryl groups on triorganoboranes are known to undergo ready exchange in the presence of catalytic amounts of boron hydrides at room temperature or below (8, 20). This reaction is also catalyzed by aluminum trialkyls (9).

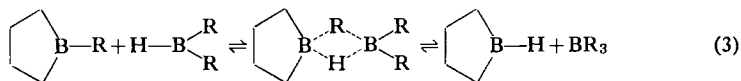
While boron atoms migrate during thermal isomerization (see Section II.B.), the nature of the boron-carbon bond remains the same during catalytic exchange.



The rate of equilibration depends on the nature of the alkyl groups involved (8, 20). Primary alkyls, such as 1-propyl, react through an electron-deficient bond (I) faster than secondary groups, such as 2-propyl.



Under similar conditions, B-alkylboracyclanes also undergo alkyl exchange. The heterocyclic ring, being exceptionally stable, does not take part in the reaction (8).



A mixture of B-ethylboracyclanes containing five-, six-, and seven-membered rings reacts with tri-1-propylborane in the presence of catalytic amounts of B_2H_6 or alkylidiboranes to give B-1-propylboracyclanes in the same ratios as in the starting materials (see Fig. 1).

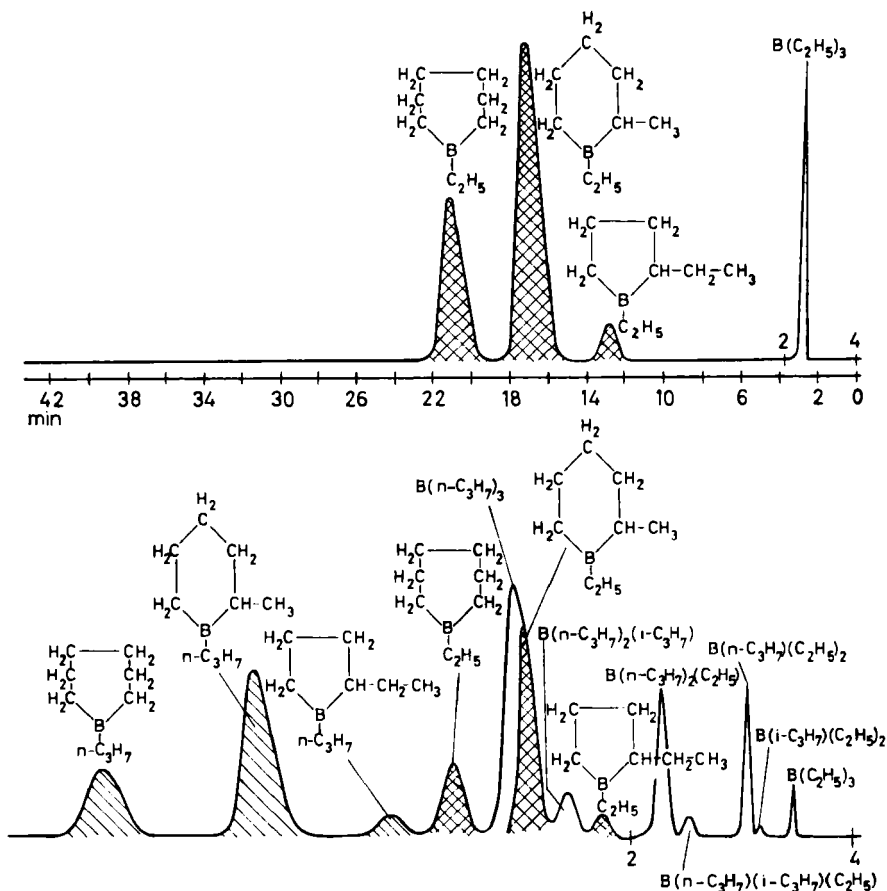
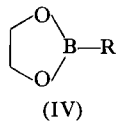
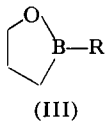
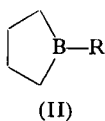


FIG. 1. Exchange of alkyl groups between B-alkylboracyclanes with 5-, 6-, and 7-membered rings. Column: 2 meters, squalane on Chromosorb 0.3–0.4 mm; carrier gas: helium, 100 ml/min; inlet pressure: 0.7 atg; temperature: $100^\circ C$; sample size: 10–15 μl .

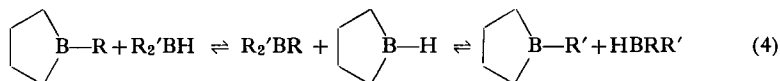
The slower exchange of secondary alkyl groups compared to primary groups is due mostly to steric factors, although inductive effects may also play a role. As the number of atoms having free electron pairs increases, the tendency to form an electron-deficient bridge between two borons decreases.

The rates of alkyl exchange vary widely for borolanes (II), 1,2-oxaborolanes (III), and 1,3,2-dioxaborolanes (IV). Primary alkyl groups exchange in seconds in (II), but require several minutes in (III), and days in (IV).

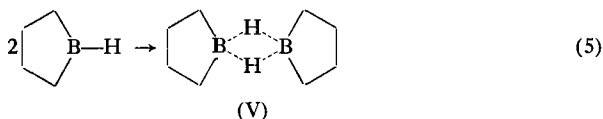


Bis(boracyclopentanes) [bis(borolanes)] (10) (V) are completely associated at room temperature. There is no alkyl exchange at low temperatures, even with catalyst present. If the concentration of boron hydrides is small in relation to the concentration of borolanes or to the ratio of borolane:alkyl groups, then (V) will exchange only at elevated temperatures. Sometimes it is more profitable to use aluminum alkyls, which form mixed associates with aluminum and boron in the electron-deficient bridge. Five-membered boron heterocycles may often be prepared with only small amounts of boron hydrides. Inhibition of alkyl exchange through the formation of bis(borolanes) is unlikely. This may be illustrated by the following considerations.

The exchange reactions may be considered as a type of "chain reaction" (4).



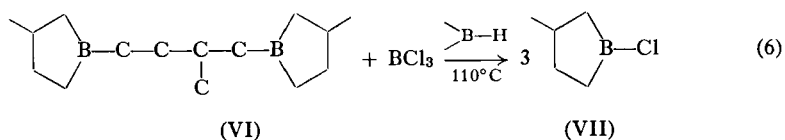
Monomeric borolanes are formed as active intermediates. Dimerization is slow if the alkyl concentration is high, and only small portions of the catalyst will be lost through the formation (5) of stable (V).



Aluminum alkyls should always be used as exchange catalysts if olefinic groups [except α -unsaturated alkenyls (11)] are attached to boron (20). Alkenyl-boranes undergo hydroboration readily at low temperatures, thus destroying the catalyst.

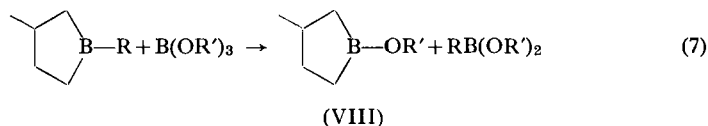
The boron hydride-catalyzed exchange reaction is not limited to triorganoboranes or boron heterocyclics. Boron trihalides readily exchange with organoboranes at low temperatures (12). Reaction of BCl_3 with 1,4-

bis(3'-methylboracyclopentyl)2-methylbutane (VI) gives high yields of B-chloro-3-methylborolane (6).



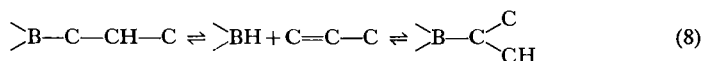
In this case the temperature must be kept above 100°C ; otherwise, because of the high concentration of (VI) the yield of (VII) will be reduced through the formation of inactive bis(borolanes) (V).

Trialkoxyboranes may be reacted with B-alkylborolanes and other boron heterocyclics in the presence of boron hydrides to give B-alkoxyborolanes (VIII) (12, 13).



B. Thermal Isomerizations

Trialkylboranes will isomerize at temperatures above 100°C through a dehydroboration-hydroboration equilibrium to form a mixture of triorganoboranes with primary and secondary alkyl groups (8, 14, 15). The $\text{B}-\text{C}_{\text{prim}}$ bond is strongly favored.



Alkyl groups with a $\text{B}-\text{C}_{\text{tert}}$ bond have not been found in these mixtures; they undergo ready dehydroboration at room temperature to form $\text{B}-\text{C}_{\text{prim}}$ and $\text{B}-\text{C}_{\text{sec}}$ linkages (16, 17).

The rate-determining step for this equilibration is the separation of olefin (dehydroboration) (18). Addition of $\text{B}-\text{H}$ bonds to olefins (hydroboration) is very rapid at room temperature (15, 19, 20, 21, 45), while dehydroboration generally does not become significant until 100°C . Compositions of equilibrium mixtures (see Table I) of simple triorganoboranes may be determined by gas chromatography (5, 6, 22). The course of

the equilibration may also be followed by gas chromatography, as illustrated in Fig. 2.

TABLE I
EQUILIBRIUM MIXTURES OF TRIALKYLBORANES AT 160°C

Tri- <i>n</i> -propylborane	Tri- <i>n</i> -butylborane
83 % <i>nnn</i>	94 % <i>nnn</i>
16 % <i>nni</i>	6 % <i>nns</i>
1 % <i>niï</i>	0 % <i>nss</i>
<i>n</i> = 1-propyl	<i>n</i> = 1-butyl
<i>i</i> = 2-propyl	<i>s</i> = 2-butyl

The proportion of B—C_{sec} bonds may be increased somewhat by raising the temperature; for example, tri-*n*-propylborane at 160°C has a ratio of 16:1 for 1-propyl to 2-propyl groups, while at 220°C, it is 12:1 (9). Trialkylboranes having long alkyl groups give primarily 1-alkylboranes, with small amounts of 2-alkylboranes. The boron is almost never bonded to a more central carbon atom.

Simple boron heterocycles, such as B-alkylboracyclanes, give equilibrium mixtures similar to trialkylboranes (8, 19, 20, 23). The alkyl groups them-

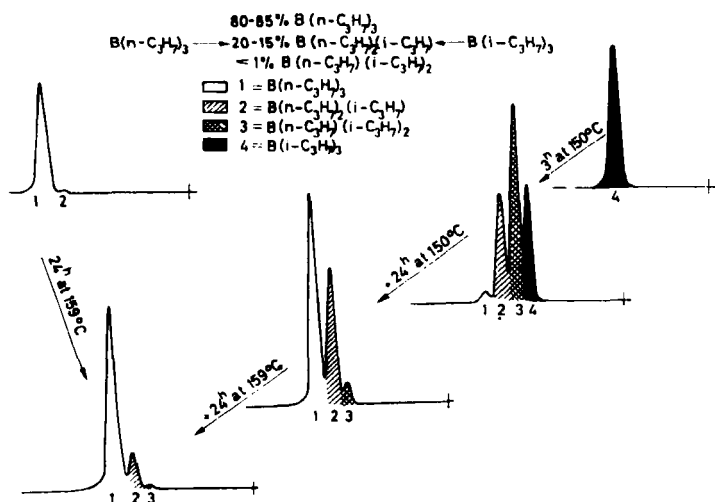


FIG. 2. Isomerization of tripropylborane. Column: silicone oil DC 710 on Chromosorb 0.3–0.4 mm; carrier gas: helium 105 ml/min; sample size: 4 μ l.

selves tend to isomerize, and the equilibrium amount of secondary groups is higher than in open-chain boranes, probably due to steric effects (24). Thus *n*-butylborolane at 160° C gives about 15% of the secondary butyl isomer, as compared to 6% for the third group of tri-*n*-butylborane.

Besides the isomerization of the B-alkyl groups, additional isomerization occurs in boron heterocyclics, giving different ring sizes. As in side-chain rearrangements, steric factors play an important role in determining the equilibrium composition of the various ring systems. There are always several different boracyclanes in equilibration with one another at elevated temperatures, due to ring contraction or expansion. Five-, six-, and seven-membered rings are all formed. Furthermore, ring-restricted stereoisomers are also found (19,20, 26, 69).

Relative stabilities of different ring systems depend both on the type of boron-carbon bonding and on the size of the ring. The boracyclane having a six-membered ring with two B—C_{prim} or one B—C_{prim} and one B—C_{sec} bond is the most stable form at elevated temperature. Table II shows the composition of various equilibrium mixtures. The stabilizing influence of ring size can be so great that, in certain exceptionally favorable examples, a B—C_{tert} bond may be formed.

TABLE II
B-ETHYLBORACYCLANE DISTRIBUTIONS AT 160° C IN EQUILIBRIUM^a

Diene	Five-membered ring	Six-membered ring	Seven-membered ring
Isoprene	100	—	—
2,3-Dimethyl-1,3-butadiene	30:70 ^b	—	—
1,4-Pentadiene	2.8	97.2	—
1,5-Hexadiene	1.0/2.7 ^b :3.8	79.9	12.6
2,5-Dimethyl-1,5-hexadiene	66.3 ^b	23.0 ^c	10.7

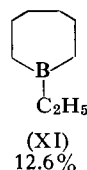
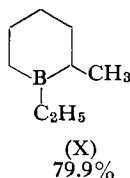
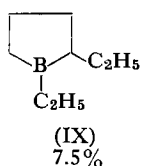
^a Gas-chromatographic analysis.

^b *Cis-trans* isomers.

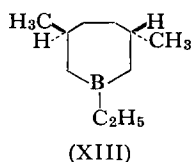
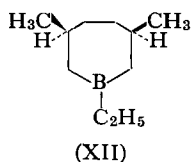
^c Contains an unknown amount of a borepane isomer.

Reaction of 1,5-hexadiene with H₂B₂(C₂H₅)₄ at low temperatures gives (C₂H₅)₃B and a mixture of boracyclanes, C₂H₅BC₆H₁₂, containing no five-membered rings. A dehydroboration step is apparently necessary to form the five-membered ring, and this proceeds at a measurable rate only

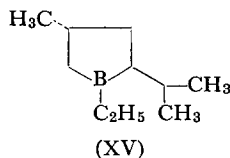
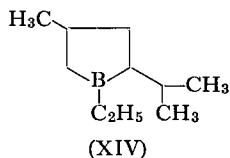
above 120° C. The principal product (97 %) is B-ethylboracycloheptane (XI); traces (3 %) of B-ethyl-2-methylboracyclohexane (X) are also found. If this reaction is run at 160° C, B-ethyl-2-ethylborolane (IX) appears in the mixture.



2,5-Dimethyl-1,5-hexadiene reacts with $\text{H}_2\text{B}_2(\text{C}_2\text{H}_5)_4$ in the cold to form a 1:1 mixture of the *cis* and *trans* isomers of B-ethyl-3,6-dimethylboracycloheptane (XII, XIII) (25).



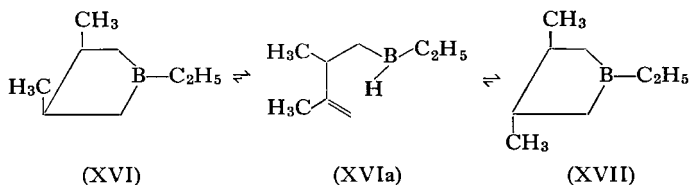
This 1:1 mixture reacts further above 120° C, changing the proportions of the isomers and forming a six-membered ring compound. After 3 hours at 120° C, the five-membered ring compound appears; at 160° C, this becomes the primary constituent. It also exists as *cis-trans* isomers (XIV, XV) which may be separated by gas chromatography.



Oxidation and subsequent hydrolysis of the boracyclane mixture gives 1,4-diols, 1,5-diols, and 1,6-diols. The 1,5-diol can only arise from a six-membered boron heterocyclic if a tertiary alkyl group is attached to the boron.

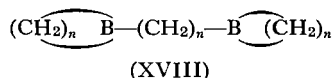
Another example of the formation of isomers is the borolane prepared from 2,3-dimethylbutadiene and $\text{H}_2\text{B}_2(\text{C}_2\text{H}_5)_4$ (20, 26, 69). At low temperatures, a 1:1 mixture of the *cis* and *trans* isomers of B-ethyl-3,4-dimethylborolane (XVI, XVII) (b.p. 55–56° C/50 mm) is formed. Heating for 6 hours

at 160°C changes the isomeric ratio to 3:7; a borohydride intermediate (XVIa) is probably formed.



This observed shift in the equilibrium composition is probably due to differences in the rates of dehydroboration of the two isomers, since hydroboration should proceed at the same rate for both isomers. Such rate differences might arise from the differing influences that the two methyl groups in the *cis* and *trans* positions exert on the borolane ring.

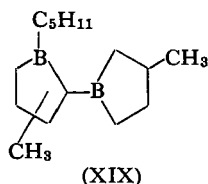
Bis(boracycyl)alkanes (23, 27), formed by the hydroboration of diolefins with B_2H_6 (23) at room temperature or from trialkylamine boranes at high temperatures (27), isomerize in the same way as B-alkylboracyclanes when heated. The equilibrium mixture of $B_2(C_nH_{2n})_3$ (XVIII) ($n = 5, 6$) was determined, before and after thermal isomerization, by oxidation and hydrolysis to diols (23).



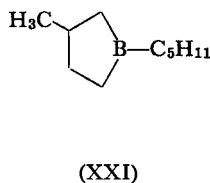
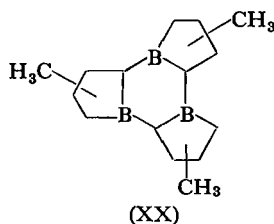
Boracyclanes, obtained from 1,4-hexadiene or 1,5-hexadiene and B_2H_6 in the cold, heated to 160°C, oxidized and hydrolyzed, gave two-thirds 1,5-alkanediol and one-third 1,6-alkanediol. The 1,5-alkanediol arose from the heterocyclic ring, while the 1,6-alkanediol came from the connecting hydrocarbon chain. Boracyclanes from B_2H_6 and 1,3-pentadiene or 1,4-pentadiene in the cold gave products as above, but the boracycpane from 1,5-hexadiene (23) and B_2H_6 in the cold gave primarily 1,6-hexanediol, indicating that a seven-membered ring containing two B—C_{prim} bonds was formed. Hardly any six-membered rings were formed under these conditions, but heating to 150–170°C gave six-membered rings.

Exact determination of the thermal equilibrium mixture from (XVIII), and also, in general, for mixtures of compounds with more than one boron atom, is more difficult than for simple B-alkylboracyclanes, because direct gas chromatographic separation is almost impossible, due to the low vapor pressures and the high thermal instability of the compounds.

Pyrolysis of (XVIII) may also cause ring isomerization involving the migration of a borolane unit into the hydrocarbon chain between the two boron atoms. This rearrangement can also occur in the isomerization of 1,4-bis(3'-methylborolanyl)2-methylbutane (VI), but is accompanied by disproportionation of alkyl groups (28), forming mono- and trifunctional groups from difunctional groups. (VI), when heated, gives a compound of the following structure (XIX):

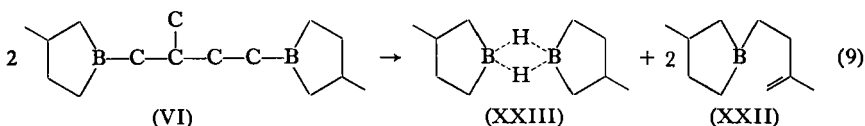


Further heating of (XIX) yields a compound of molecular weight 240, which has three boron atoms and is apparently a triboracyclohexane derivative (XX) (28).

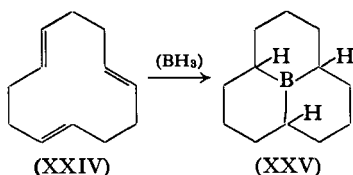


A further disproportionation product is isopentyl-3-methylborolane (XXI).

The first step of this reaction, the dehydroboration of (VI), can be realized separately. At 150°C and reduced pressure, B-isopentenyl-3-methylborolane (XXII) and bis(3-methylborolane) (XXIII) may be isolated.



Hydroboration of all-*trans*-cyclododeca-1,5,9-triene (XXIV) leads to *cis*-perhydro-9b-boraphenylene (XXV) (30, 31).



Heating (XXV) for several hours at 200° C in the presence of a tertiary amine under a hydrogen atmosphere causes isomerization. Whereas (XXV) boils at 110° C/9 mm, the other isomer, *cis,cis,trans*-perhydro-9b-bora-

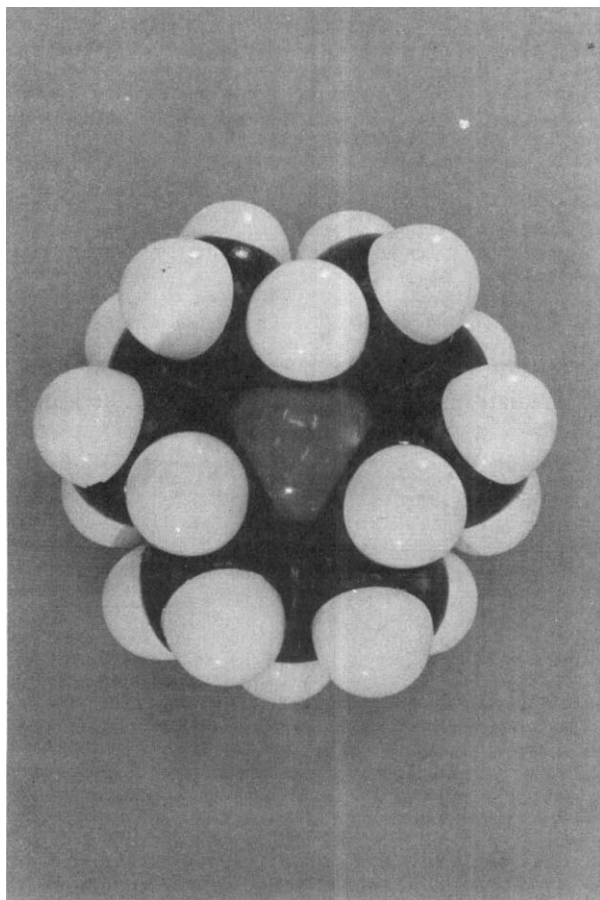
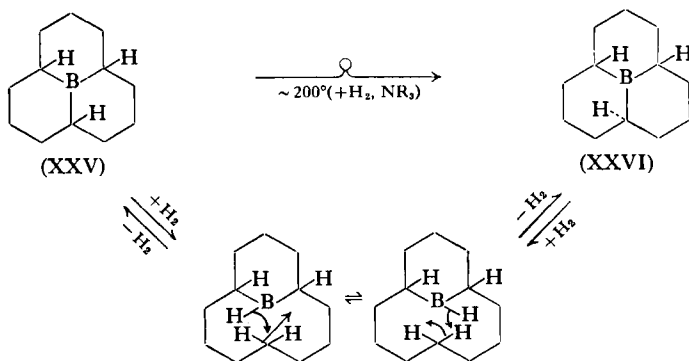


FIG. 3. *cis,cis,cis*-Perhydro-9b-boraphenalene (XXV).

phenalene (XXVI) is a crystalline solid melting at 31° C (24, 31). Hydrogen and amine are not used up in the reaction. Isomerization must occur by hydrogenation of a boron-carbon bond (32, 33), followed by configuration rearrangement and transannular dehydrogenation (see Figs. 3 and 4).

The infrared spectra of (XXV) and (XXVI) are given in Figs. 5 and 6; the compounds may be distinguished from each other by the spectra (24).



This isomerization can occur because the amine stabilizes the boron-hydrogen intermediate. Heating under hydrogen in the absence of amine

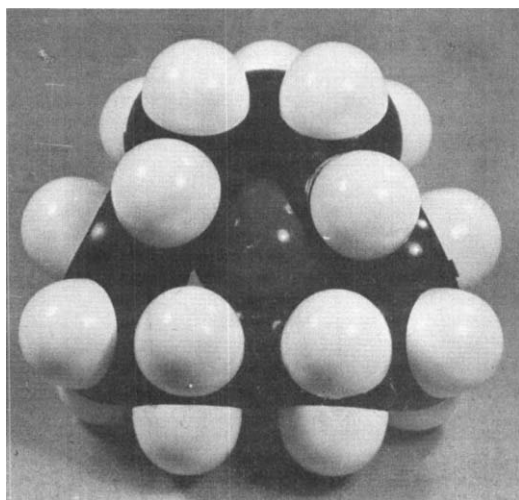


FIG. 4. *cis,cis,trans*-Perhydro-9b-boraphenalene (XXVI).

splits the carbon-boron bonds, yielding saturated hydrocarbons, such as cyclododecane, methane, ethane, propane, butane, etc. Simple heating of (XXV) or (XXVI) does not give isomerization either. Dehydroboration

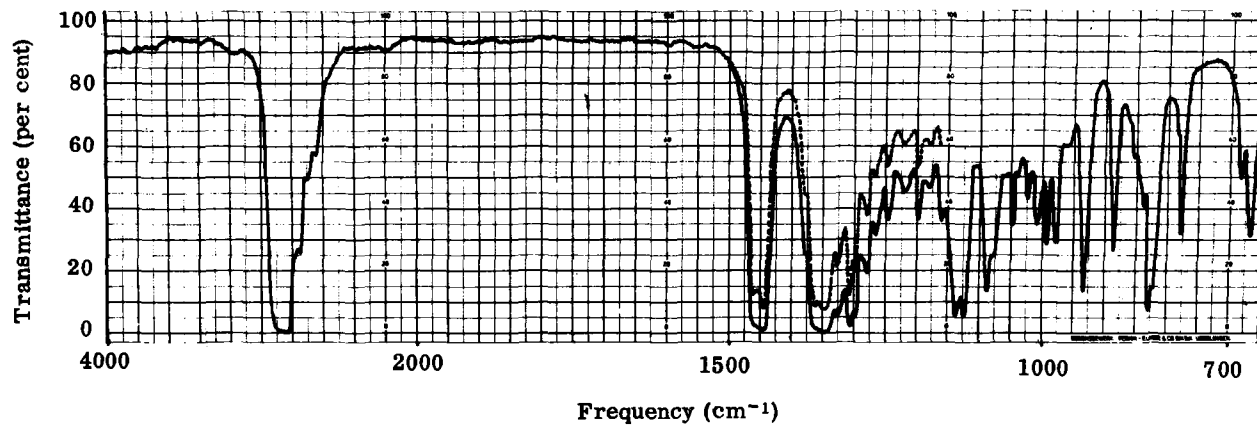


FIG. 5. Infrared spectrum of all-*cis*-perhydro-9b-boraphenalene (XXV). Solid line: $d = 0.05$ mm (NaCl prism); dashed line: $d = 0.025$ mm (NaCl prism).

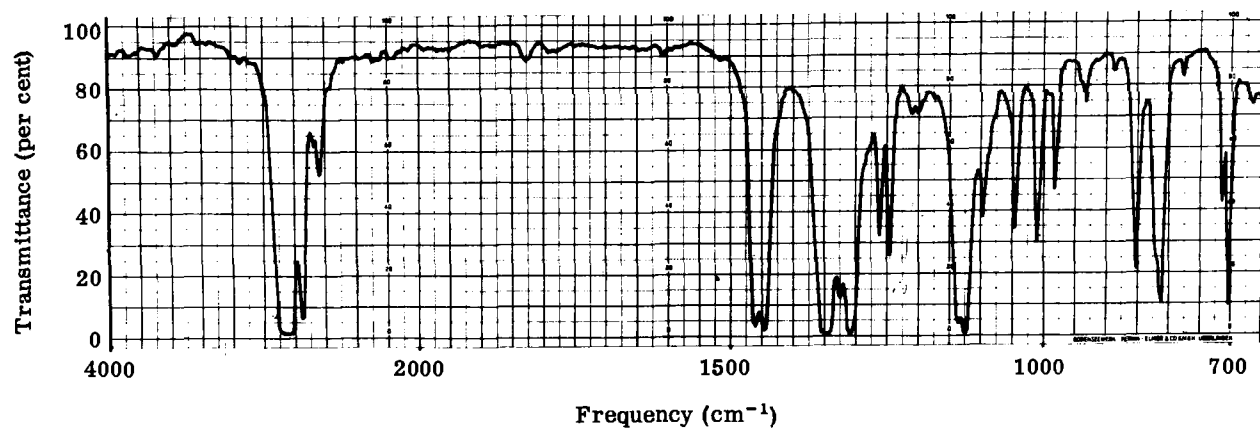
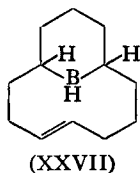


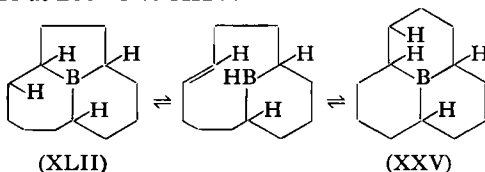
FIG. 6. Infrared spectrum of *cis,cis,trans*-perhydro-9b-boraphenalene (XXVI); $d = 0.05$ mm (NaCl prism).

begins at elevated temperature, and the intermediate 13-borabicyclo[7.3.1]-tridecene (XXVII) is apparently irreversibly destroyed.



This example indicates the limit of the reversible thermal isomerization of organoboranes.

13-Boratricyclo[6.4.1.0^{4,3}]tridecane (XLII) which is formed during the hydroboration of *trans,trans,cis*-cyclododeca-1,5,9-triene and probably has an all-*cis* arrangement of the hydrogens at the boron-bonded carbon atoms (24, 31) isomerize at 200° C to XXV.



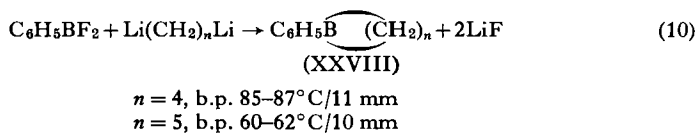
This also demonstrates the preference for six-membered boron heterocyclic rings in isomerization reactions.

III

SYNTHESES OF HETEROCYCLIC ORGANOBORANES WITH ONE BORON ATOM

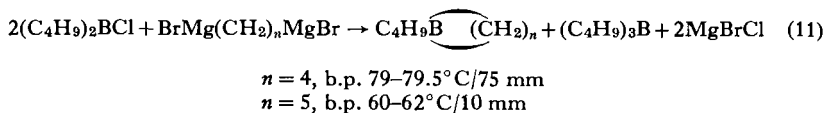
A. Reaction with Organometallic Compounds

The first synthetic method developed for preparing boron-carbon rings involved the use of organometallic compounds (1). Currently, this preparation is only of historical interest, so far as alkylboron compounds are concerned, but it is still important in the synthesis of arylborane heterocyclics. $C_6H_5BF_2$ and α,ω -dilithioalkanes react to form simple B-phenylboracyclanes (XXVIII).

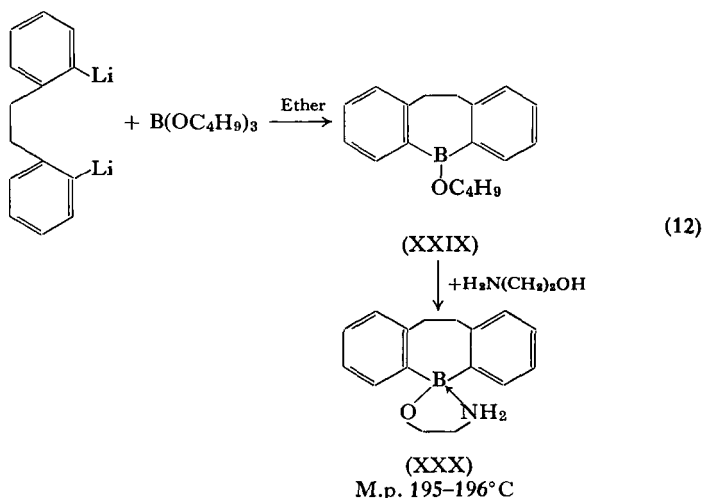


B-phenylborolane may be obtained in 45 % yield as an ethereal solution. Its stability to disproportionation is remarkable, for arylalkylboranes, ArBR_2 , readily disproportionate to Ar_3B and R_3B (34, 35).

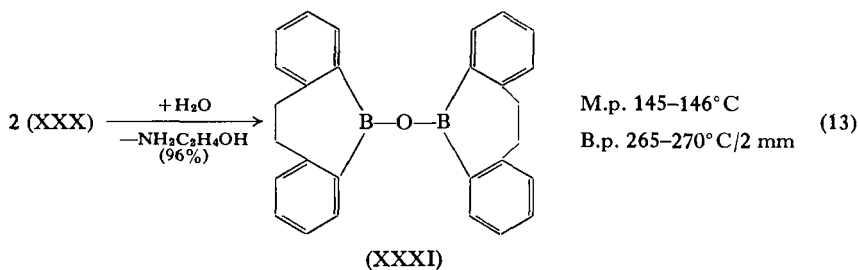
Bifunctional Grignard reagents may also be used for the synthesis of boron heterocyclics (36–39). Reaction of $(n\text{-C}_4\text{H}_9)_2\text{BCl}$ with the di-Grignard of $\text{Br}(\text{CH}_2)_n\text{Br}$ ($n = 4, 5$) gives B-*n*-butylboracyclanes.



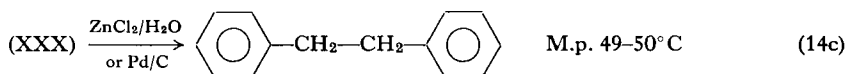
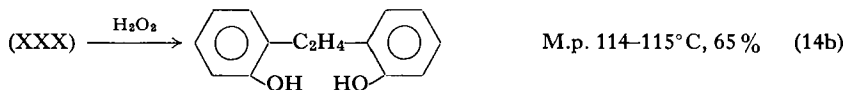
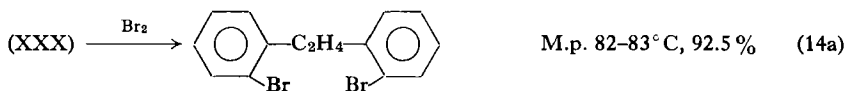
Organolithium compounds may be used to prepare boron heterocyclics containing B— C_{aryl} bonds. Derivatives of dibenzodihydroborepins may be prepared from tributoxyborane and *o,o'*-dilithiodibenzyl (40).



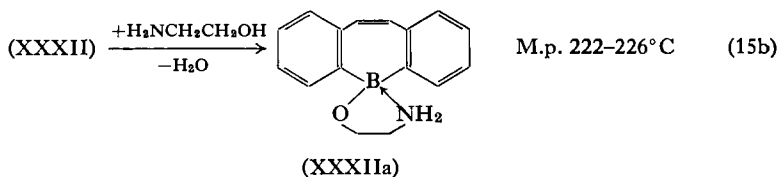
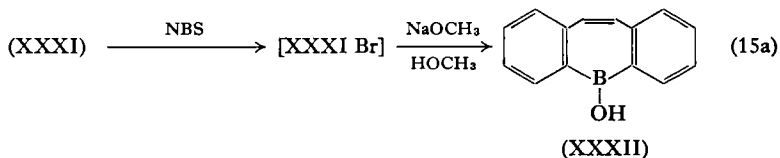
5-(2'-aminoethoxy)-10,11-dihydro-dibenzo [b.f] borepin (XXX) is easily isolated in pure form. It hydrolyzes to give the anhydride (XXXI).



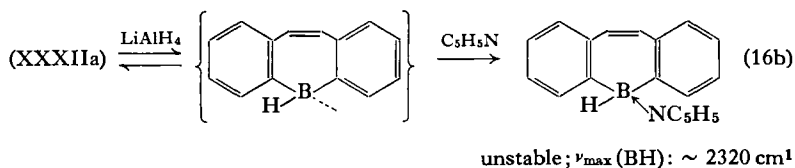
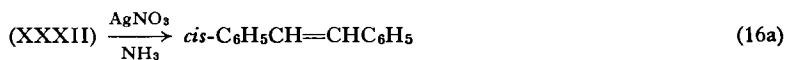
The structure of (XXX) was determined by the following reactions (40):



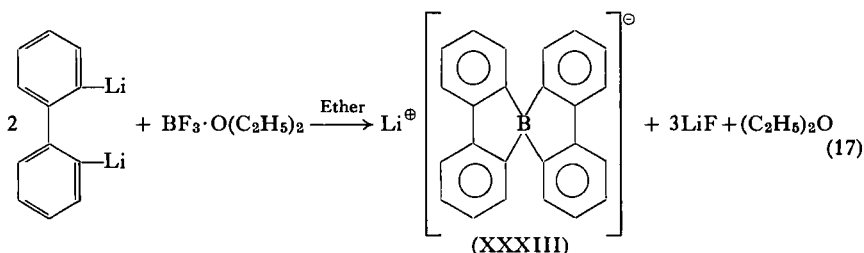
(XXXI) may be brominated with *N*-bromosuccinimide (NBS) and treated with NaOCH₃ in CH₃OH to give 5-hydroxydibenzo[b,f]borepin (XXXII), which is of theoretical interest due to the possible aromatic character of the borepin ring (41, 42).



The structure of (XXXII) was determined by the following reactions (41, 42):

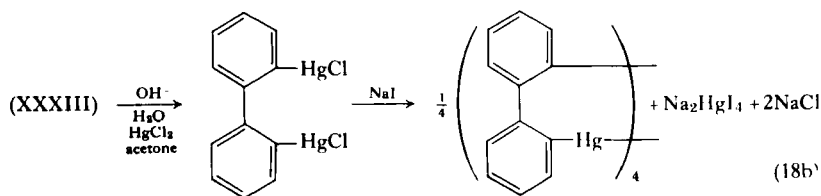
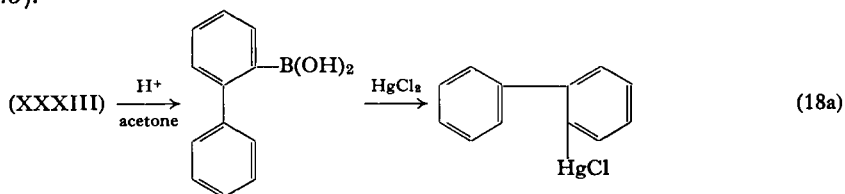


The complex anion (XXXIII) is the first known example of a boron heterocyclic having a spiro boron atom (43, 44). 2,2'-Dilithiobiphenyl and $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ give (XXXIII) in 44 % yield (43).

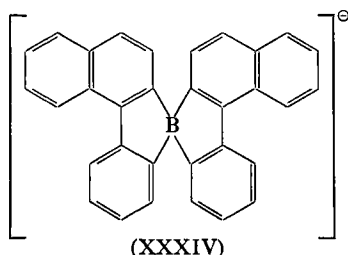


(XXXIII) resembles tetraphenylboranate anion $\text{B}(\text{C}_6\text{H}_5)_4^-$ in its properties, although precipitation reactions with large, monovalent cations are not as sensitive, probably because of the rigid structure of (XXXIII). The two biphenyl groups lie in mutually perpendicular planes. Precipitation of the tetra-methylammonium salt of (XXXIII) (m.p. 370°C) from aqueous solution is one way to get the complex ion in pure form.

This spiro complex undergoes certain cleavage reactions, from which some information on the $\text{B}-\text{C}_{\text{aryl}}$ bond stability may be gotten. Reaction of $(\text{CH}_3)_4\text{N}^+(\text{XXXIII})^-$ in acidic medium (acetone–water mixture) yields *o*-biphenylboronic acid, which reacts with mercuric chloride to form 2-biphenylmercuric chloride (m.p. $162.5\text{--}163^\circ\text{C}$). However, treatment of (XXXIII) with HgCl_2 in aqueous, “alkaline acetone” forms 2,2'-bis-(chloromercuri)biphenyl (m.p. $246\text{--}247.5^\circ\text{C}$), which may be treated with NaI to give 2,2'-biphenylmercury (43a). In acidic solution, only one $\text{B}-\text{C}_{\text{aryl}}$ bond is maintained, whereas the cleavage is incomplete in base (43).



The spiro-asymmetric anion (XXXIV) has been resolved into optical antipodes as its methylpropylphenylbenzylammonium salt (39).

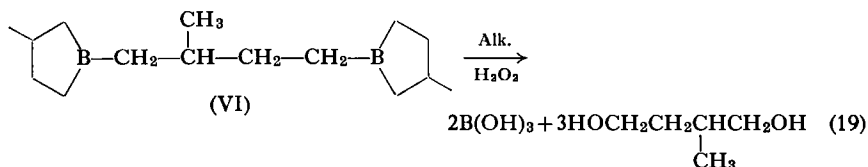


This indicates that the central boron atom is tetrahedral.

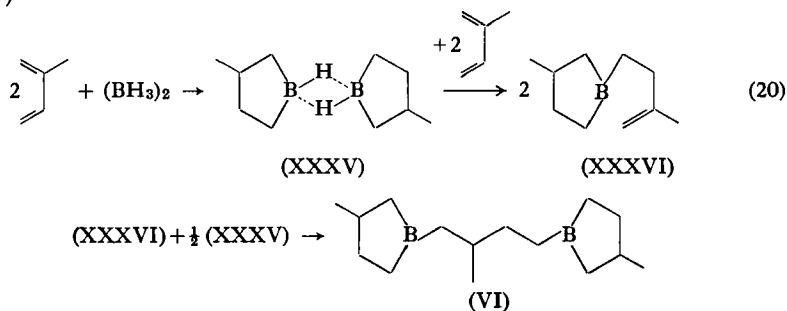
B. Hydroboration

Many aliphatic boron heterocyclics can be readily prepared by hydroboration of dienes or polyolefins (30, 45–49). Complete reaction of C=C bonds in polyolefins, such as butadiene, isoprene, 1,5-hexadiene, and cyclododecatrienes, yields colorless liquids which are distillable in many cases under reduced pressure (30, 45–49).

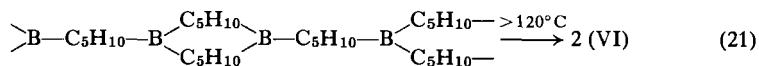
Butadiene and similar olefins undergo hydroboration to form compounds of type (XVIII) (see Section II.B.) (23, 27, 45, 48). Like other bis(boracycyl)-alkanes, they can be oxidized and hydrolyzed to yield three moles of alkanediols, e.g.,



Bis(boracyclanes) (XXXV) (10, 27, 48) and B-alkenylboracyclanes (XXXVI) (27, 48) are formed as intermediates.

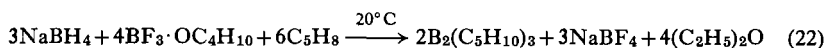


Polymeric products are also obtained; the quantity depends on the type of diene and the experimental conditions. Heating above 120° C degrades a large part of the high-viscosity polymers into distillable boron heterocyclics through a dehydroboration-hydroboration equilibrium (10):



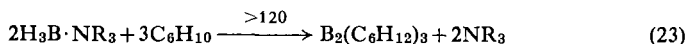
Polymer formation usually arises from side reactions, in which the diene, because of hydrogen migration, serves as a monofunctional and trifunctional, as well as a difunctional, group. For example, isoprene and triethylamineborane react to form a distillable compound whose molecular weight suggests a diborolanylalkane, but whose structure is (XIX). Further heating causes disproportionation to (XX) and (XXI) (see Section II.B.).

Hydroboration of alkenes may be carried out under many different experimental conditions. Gaseous B_2H_6 may be used in solution (tetrahydrofuran, diglyme, triglyme) (49, 50) or as the amine or some other complex derivative. These complexes release the active borane *in situ*. Certain reagents, such as $\text{NaBH}_4/\text{BF}_3 \cdot \text{OR}_2$ or $\text{BH}_3\text{NR}_3/\text{BF}_3 \cdot \text{OR}_2$, allow hydroboration at room temperature. Isoprene reacts readily with NaBH_4 and $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in diglyme or triglyme at 20° C (49, 50).



1,4-Bis(3'-methylboracyclopentyl)-2-methylbutane is obtained in 80% yield (51). The intermediate free borane, *in statu nascendi*, adds immediately to the $\text{C}=\text{C}$ bonds. All the hydrogens of NaBH_4 are used. Filtration removes NaBF_4 and fractional distillation removes solvent, leaving the pure product (51).

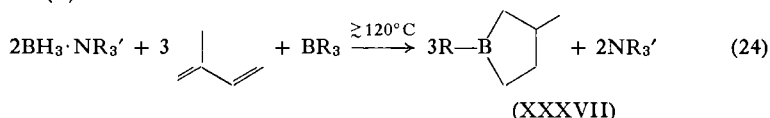
The work-up of the reaction mixture from trialkylamineboranes and dienes is more simple (16, 24, 30, 45, 47, 48). High temperatures (120–150° C) must be used, however, for quantitative yields.



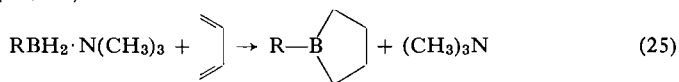
The reaction with 1,5-hexadiene gives an isomeric mixture of bis(boracycyl)alkanes in 70–90% yield; these isomers differ in the position of the boron atoms on the hydrocarbon chain and in the ring size. Isoprene gives more uniform products than butadiene. Hydroboration cannot be done at

very high temperatures, because of the irreversible rearrangement of the boron heterocyclic; hydrogen gas is split off above 200°C. This process may sometimes be used to make new polycyclic boranes (cf. Section III.D.).

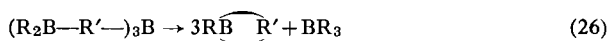
B-alkylboracyclanes (XXXVII) may be readily prepared by reaction of dienes with trialkylamine-borane, in the presence of trialkylboranes, at 120–140°C (8).



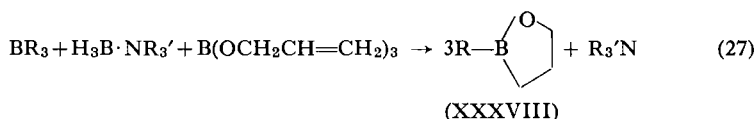
Trialkylamine-dialkylboranes (formed from $\text{B}_2\text{H}_2\text{R}_4$ and $\text{R}_3'\text{N}$) will react with dienes at low temperatures, in spite of the stabilizing influence of the amine (21); rate studies showed that $(\text{C}_2\text{H}_5)_3\text{NB}(\text{C}_3\text{H}_7)_2\text{H}$ reacts rapidly with monoolefins at room temperatures to form trialkylboranes (20, 21). This is also true with di- and polyolefins. Trialkylamine-monoalkylboranes react more slowly, because of the greater stability of the complex, but heating above 60°C with mono- or polyolefins gives the corresponding trialkylboranes (52, 53).



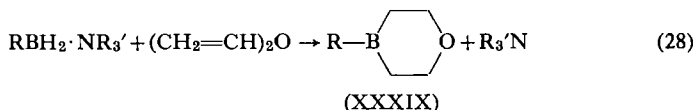
The B-alkylboracyclanes are the most stable products under these conditions, because an alkyl exchange is possible in the presence of BH compounds. Therefore, above 120°C, polymeric organoboranes are transformed, partly because of the dehydroboration-hydroboration equilibrium of B-alkylboracyclanes and other lower organoboranes, e.g.,



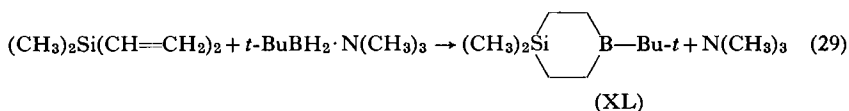
In addition to diolefins, there are other bifunctional compounds that will form boron heterocyclics under analogous reaction conditions. For example, the triallyl ester of orthoboric acid reacts with trialkylamine-borane in the presence of trialkylboranes to give B-alkyl-1,2-oxaborolane (XXXVIII) (8).



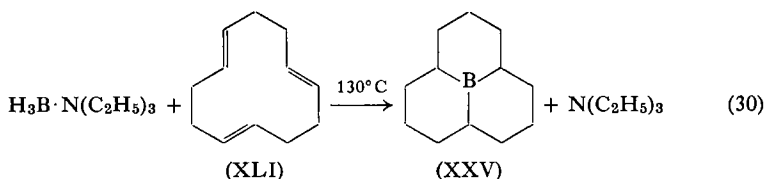
Similarly, trialkylamine-alkylboranes react with divinyl ether to give B-alkyl-1-oxa-4-boracyclohexane (XXXIX) (52, 53).



Dimethyldivinylsilane reacts in the same manner with trimethylamine-*t*-butylborane to give 1-sila-4-boracyclohexane (XL) (52, 53).



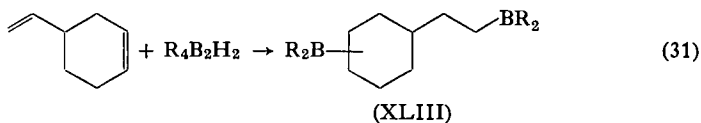
Trialkylamine-boranes will also react with polyolefins to form boron heterocyclics; in special cases, the products can be distilled. Triethylamine-borane reacts with cyclododeca-1,5,9-trienes to form perhydro-9b-boraphenalenenes (30, 31, 31a, 45, 47, 48).



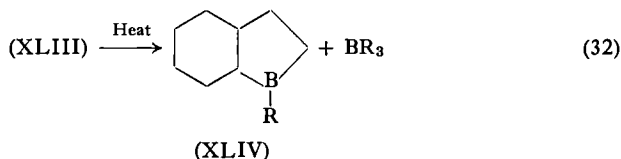
All-*trans* cyclododeca-1,5,9-triene (XLI) gives the all-*cis* perhydro-9b-boraphenalene, while *trans,trans,cis*-cyclododeca-1,5,9-triene gives 13-boratricyclo[6.4.1.0^{4,13}]tridecane (XLII) (see Section II, B) (31). Alkyl-diboranes can often be used as effective substitutes for diborane or trialkylamine-boranes in the hydroboration of polyolefins (19–21, 54, 55); this is also true of aryl-diboranes (56). Ethyl- and propyldiboranes, B₂H_{6-n}R_n, are particularly favorable (19–21). They are easy-to-handle liquids which react at low temperatures and are more selective toward C=C addition than diborane (19, 20). The alkyl groups do not make the work-up any more difficult.

From mixed alkylethylboranes, arising from ethyldiboranes, all ethyl-boron groups may be removed as (C₂H₅)₃B by addition of small amounts of borohydrides (8, 20) or aluminum trialkyls (9), or by use of di- or polyolefins at room temperature and reduced pressure. In this way, yields

of boron heterocyclics having five-, six-, and seven-membered rings may be increased (19, 20). Whereas butadiene and isoprene give predominantly five-membered heterocyclics, 1,4-pentadiene and ethyldiborane at room temperature give primarily B-ethylboracyclohexane, with small amounts (10%) of B-ethyl-2-methylborolane (20). 2,3-Dimethylbutadiene reacts with ethyldiborane at room temperature to give a 1:1 mixture of (XVI) and (XVII) (see Section II, B). 4-Vinylcyclohexene gives a doubly borylated product (XLIII) with alkyldiboranes (82, 83).

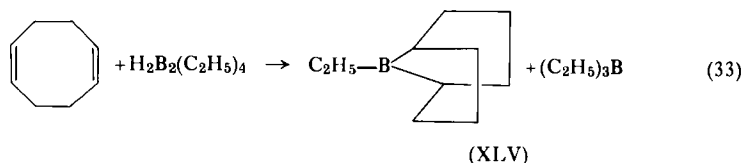


Heating of (XLIII) causes disproportionation, giving 1-borahydrindane (XLIV) (83).

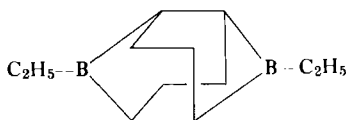


$(\text{C}_2\text{H}_5)_4\text{B}_2\text{H}_2$ and 1,5-hexadiene give 97% (XI) and 3% (X) at 20° C; triethylborane is split off by disproportionation. Organoboranes of higher molecular weight are also produced. Under similar conditions, 2,5-dimethyl-1,5-hexadiene reacts to give a 1:1 mixture of (XII) and (XIII) (see Section II, B), which are easily separated by gas chromatography (25); no boracyclohexanes are formed. The boron atom is almost never attached to a tertiary carbon in the terminal C=C bond of the olefin.

The hydroboration of cyclodienes is also possible at room temperature; 1,5-cyclooctadiene reacts with $(\text{C}_2\text{H}_5)_4\text{B}_2\text{H}_2$ to give B-ethyl-9-borabicyclo-[3.3.1]nonane (XLV).

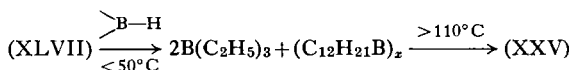
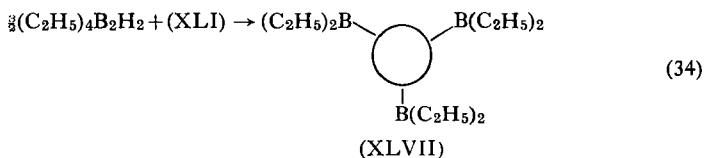


With cycloocta-1,3,5,7-tetraene one obtains, in addition to polymeric materials, B-ethyl-2,6-diboraadamantane (XLVI) in low yields.



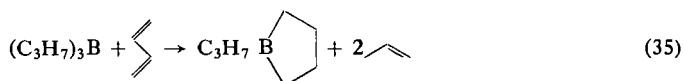
(XLVI)

$(\text{C}_2\text{H}_5)_4\text{B}_2\text{H}_2$ reacts with suitable triolefins in the same way. *cis*, *trans*, *trans*-Cyclododeca-1,5,9-triene is hydroborated gradually, with three moles $(\text{C}_2\text{H}_5)_2\text{BH}$, finally adding to give $(\text{C}_{12}\text{H}_{21})[\text{B}(\text{C}_2\text{H}_5)_2]_3$ (XLVII). The *trans* $\text{C}=\text{C}$ bonds react somewhat faster than the *cis* bonds. Removal of triethylborane in the presence of borohydrides gives a polymeric material $(\text{C}_{12}\text{H}_{21}\text{B})_x$; this, heated above 110°C , gives all-*cis*-perhydro-9b-boraphenylene (XXV) in 80% yield (b.p. $131^\circ\text{C}/16\text{ mm}$) (31).



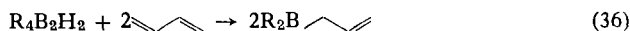
C. Displacement Reactions

Trialkylboranes, R_3B ($\text{R} > \text{C}_2$), react with dienes (27) above 120°C to give displacement (15, 33, 57) of the alkyl groups; B-alkylboracyclanes can be isolated from the mixture, e.g.,



This reaction proceeds through a borohydride intermediate, which arises from dehydroboration. As in thermal isomerization, a mixture of boron heterocyclics is obtained. Tripropyl and tributylborane are particularly suitable for displacement reactions because propene and butene are easily removed from the reaction mixture. Ethylene is not evolved under similar conditions, and triethylborane does not appear to undergo this type of reaction (33, 57).

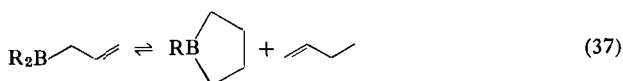
Displacement reactions with dienes proceed through various intermediates. After the initial dehydroboration the dialkylborane (R_2BH) reacts with the excess diene to form a dialkylalkenylborane.



The equilibrium constant for this reaction step has not yet been determined, but it must be very close to 1, if the $C=C$ bonds of the dienes are isolated and if they correspond to those in the monoolefins evolved.

$$\frac{[BR_3][\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2]}{[R_2B-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2][\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2]} = K \sim 1$$

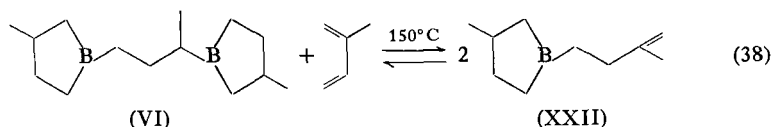
Dialkylalkenylboranes react under the same conditions in an intramolecular displacement to form boracyclanes. Experiments show that the reaction



goes from left to right if five-, six-, or seven-membered rings are formed. The equilibrium constant C is less than 1. Intermediate borohydrides play no part in the over-all equilibrium constant, since they are only present in trace quantities.

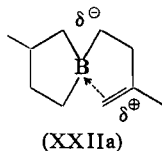
$$\frac{[BR_3][\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2]}{[R-B\text{C}_4\text{H}_7][\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2]^2} = C < 1$$

The equilibrium constant for reaction (38) is about 1. Since only about 50% of (XXII) is formed at 150°C and atmospheric pressure, the equilibrium constant must be close to 1. (XXII) boils higher than isoprene and



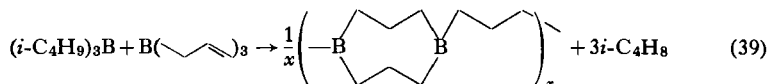
cannot be separated under the reaction conditions; the mixture must be cooled below 100°C first. There are several possible isomeric forms for the isopentenyl group in (XXII), but the 3-methyl-3-butenyl compound is

strongly favored because of stabilization from back coordination (XXIIa) (29, 69, 87)



(XXII) shows two characteristic C=C stretching bands in the infrared (see Fig. 7), at 1610 [for (XXIIa)] and 1645 cm^{-1} , and a CH_2 rocking band at 883 cm^{-1} . Treatment with NaOCH_3 (to form a complex) causes the 1610 cm^{-1} band to disappear, without affecting the 1645 cm^{-1} band; addition of $\text{B}(\text{OCH}_3)_3$ [to form $\text{NaB}(\text{OCH}_3)_4$] restores the 1610 band (28).

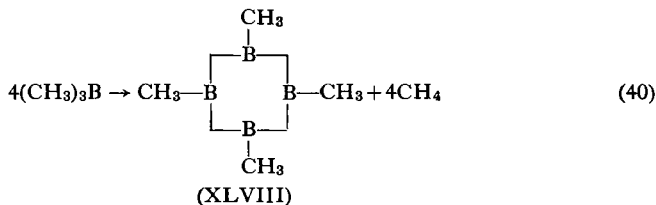
Trienes also undergo displacement reactions, forming polymeric organoboranes in most cases. all-*trans*-cyclo-dodeca-1,5,9-triene (XXIV) (58) reacts readily with $\text{B}(i\text{-C}_4\text{H}_9)_3$ to form (XXV) and isobutylene (31). A special case for the use of displacement to prepare boron heterocyclics is the reaction of triallylborane with triisobutylborane (59). At 130–140° C a 1:1 reactant ratio gives isobutylene and a polymeric product with the constitution of a 1,5-diboracyclooctane. Many other isomeric forms (such as a six-membered ring) are possible, and it is not yet known whether the eight-membered ring is the principal product.



D. Pyrolysis of Organoboranes (Irreversible Reactions)

Thermal degradation of alkyl and arylboranes gives a considerable variety of boron-containing products of different types and sizes.

The pyrolysis of $(\text{CH}_3)_3\text{B}$ has been known for several years (60). Numerous polymeric products are obtained, from which definite boron heterocyclics may be isolated, e.g., an eight-membered ring compound having alternate carbon and boron atoms (XLVIII).



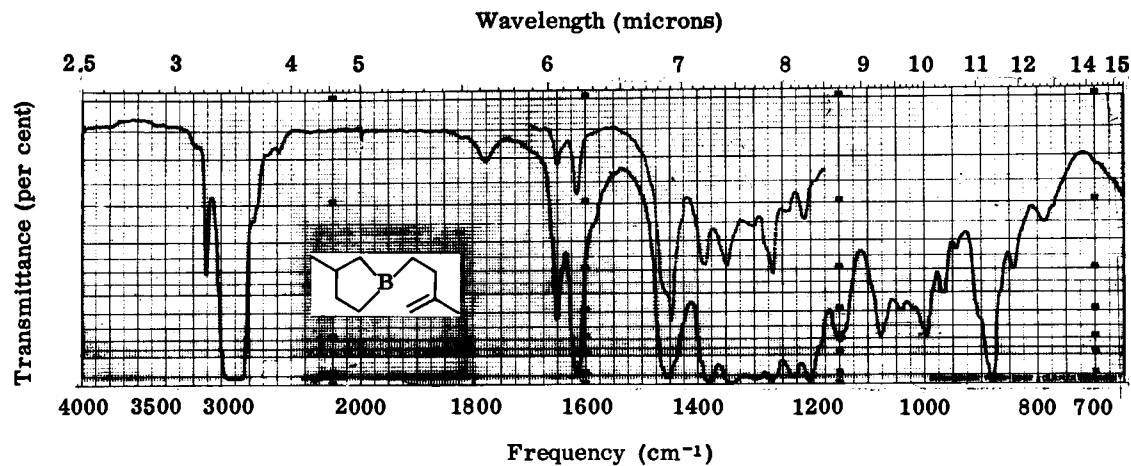
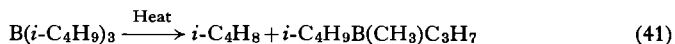
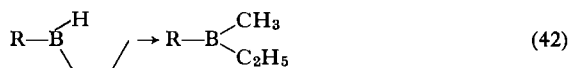


FIG. 7. Infrared spectrum of B-(3'-methyl-1'-but-3'-enyl)-3-methylborolane. Solid line: $d = 0.05$ mm (NaCl prism); dashed line: ca. 10 % in cyclohexane.

Later, systematic studies were made on the pyrolysis products of other lower trialkylboranes (24, 61–64). These reactions proceed at relatively low temperatures with surprisingly high yields. Trialkylboranes having 2 or 3 carbon atoms in the main alkyl chain (e.g., ethyl, propyl, isobutyl) rearrange at about 300° C in the presence of dialkylborohydrides to form methylboranes (62). Thus $(C_2H_5)_3B$ gives C_2H_4 and methylethylboranes, while $(i-C_4H_9)_3B$ gives isobutylene and methylpropylisobutylborane.



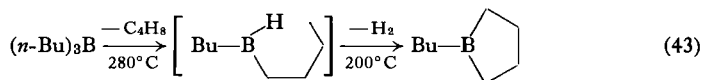
Pyrolysis gives a mixture of various mixed trialkyl boranes, because of the alkyl exchange on boron (8). For example, as a result of thermal isomerization the propyl groups on boron will be both 1- and 2-propyl. No B—H-containing products are obtained, but they appear as reactive intermediates.



1. Boracyclanes from Alkylboranes

Trialkylboranes having four or more carbon atoms in the alkyl chain give high yields of boron heterocyclics when heated to 200–300° C (24, 61, 63, 64). Generally, no products with methyl groups on boron are found; intermediate dialkylborohydrides cause hydrogen cleavage and cyclization.

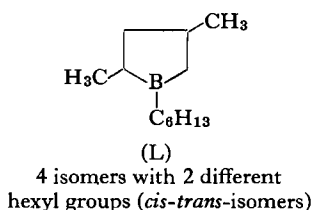
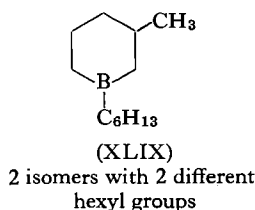
The simplest example is the pyrolysis of tri-*n*-butylborane (63). At 300° C, hydrogen and a mixture of butenes—2-butene predominating—are split off (24), and a 90% yield of B-butylboracyclopentane (b.p. 54–57° C/14 mm) is obtained; gas chromatography separates this into the two isomers: 85% 1-butylborolane and 15% 2-butylborolane (5, 24, 63).



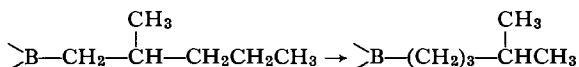
Oxidation with alkaline H_2O_2 gives 1-butanol, 2-butanol, and 1,4-butanediol.

Increasing chain lengths cause the pyrolysis products to be more complex. The longer the chain length, the lower the temperature necessary for pyrolysis (e.g., rapid loss of H_2 occurs at 280° C with tri-*n*-hexylborane, at 220° C with tri-*n*-undecylborane). Composition of these ring isomers is what would be expected from thermal equilibrium of boracyclanes (63) (see Section II.B.).

Tri(2-methyl-1-pentyl)borane evolves isohexenes (primarily 2-methyl-2-pentene) and hydrogen when pyrolyzed, forming four boron-containing isomers of formula $C_6H_{13}BC_6H_{12}$ (b.p. 98–102°C/16 mm). Isohexylboracyclohexane (XLIX) forms 80% of the product, and 20% is isohexylboracyclopentanes (L).

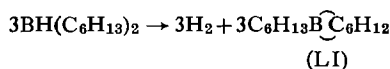
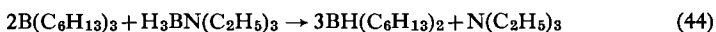


Isomers are formed by the migration of the boron along the alkyl chain, e.g.,

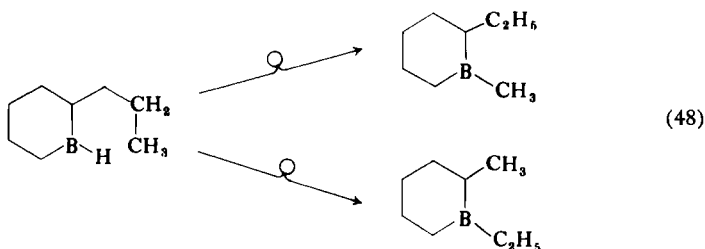


Tri(2-ethylhexyl)borane forms a rather complicated mixture of boron heterocyclics that has not yet been resolved; however, the major products appear to contain six-membered rings. There are three different chains outside of the rings: 2-ethyl-1-hexyl, 3-methyl-1-heptyl, and 5-methyl-1-heptyl (most common). Alkyl groups having the boron on a central carbon normally do not appear. Olefins formed consist almost entirely of 3-methyl-3-heptene and 3-methyl-2-heptene.

Mixture of trialkylamine-borane and trialkylborane mixtures also give boracyclanes when pyrolyzed. Et_3NBH_3 and $(C_6H_{13})_3B$ in a 1:2 ratio yield (LI) when heated to 200°C.

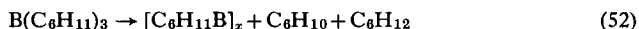


In addition to five- and six-membered rings, traces of a seven-membered ring can be found. The isomeric mixture is similar to that gotten from thermal isomerization of B-alkylboracyclanes from 1,5-hexadiene and trialkylboranes or alkyl diboranes. Oxidation and hydrolysis give primarily 1,5-hexanediol, along with the 1,4- and 1,6-diols. The side chain R is mostly

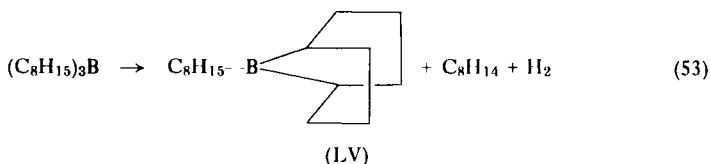


3. Endoboron Compounds from Cycloalkylboranes

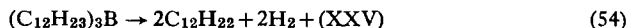
Cycloalkylboranes will also form heterocyclics by pyrolysis (24, 67). Since cycloalkenes cleave readily at fairly low temperatures (ca. 180° C), cyclization proceeds smoothly at 200° C. It is absolutely essential that the cyclic ring be large enough. Tricyclohexylborane does not form 7-borabicyclo-[2.2.1]heptane; instead, polymeric boron-containing products are formed and volatile materials evolved.



Tricyclooctylborane, though, forms B-alkyl-9-boratricyclo[3.3.1]nonane (LV) very readily. This reaction can be carried out in the presence of a trialkylborane, so that the third boron valence is saturated.



Tricyclododecylborane, when heated at 220° C, evolves two moles of cyclo-dodecene (*cis-trans* mixture) and two moles of H₂ to form all-*cis*-perhydro-9b-boraphenalene (XXV).

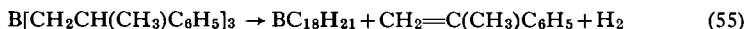


(XXV) is identical to the compound formed by hydroboration of all-*trans*-cyclodeca-1,5,9-triene (see Section III.b).

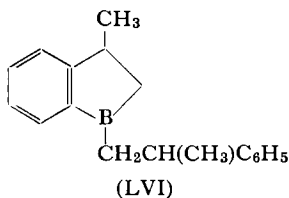
4. Preparation of Boraindanes and Boratetralins

Whereas trialkylboranes form dialkylboranes at 150° C, aralkylboranes do not form the corresponding diaralkylboranes at higher temperatures and reduced pressures. Arylalkenes and H₂ are obtained simultaneously from these compounds. Normally no B—H compounds are found in the heated products of triaralkylboranes.

One mole of tri(2-phenylpropyl)borane reacts at 180–200° C and 10⁻¹–10⁻³ mm Hg to form one mole of α-methylstyrene and H₂, along with a C₁₈H₂₁B compound—a colorless, air-sensitive liquid, b.p. 126° C/0.5 mm (68, 69).



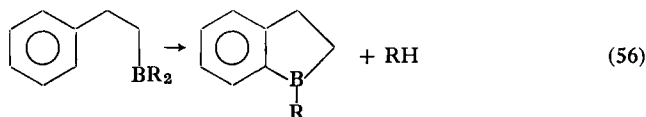
This compound has a B—C_{aryl} bond, as determined by reaction with HgCl₂ (70). Structural determination shows it to be B-(2'-phenylpropyl)-3-methylboraindane (LVI).



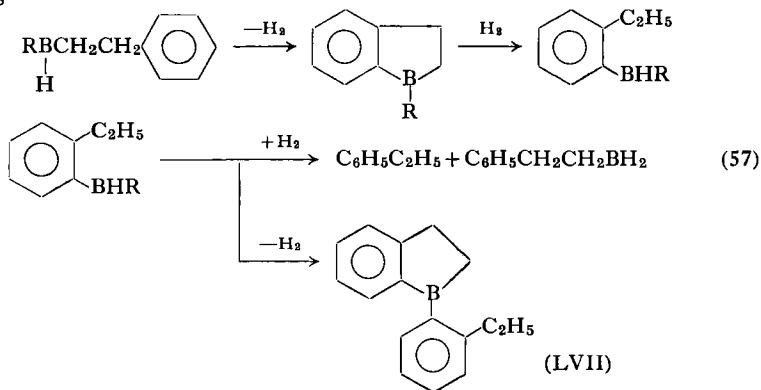
The infrared spectra of (LVI) and the analogous B-propyl compound given in Figs. 8 and 9 show the *o*-disubstituted phenyl nucleus ($\sim 750\text{ cm}^{-1}$).

Pyrolytic ring closure usually proceeds in high yields (over 90 %) to give boron heterocyclics. Necessary temperatures range between 180° and 250°C . Tri(2'-phenylethyl)borane gives B-(2'-phenylethyl)boraindane (LVIIa), forming styrene, H_2 , and ethylbenzene as by-products.

Saturated hydrocarbons apparently are formed through hydrogenation of the aralkylborane, and not through dehydrogenation of the initially formed styrene. Another way for the direct formation of hydrocarbons, such as ethylbenzene [see reaction (56)], is also possible but not very important except in special cases, because $\text{R}-\text{H}$ formation is much slower than H_2 formation from $\text{B}-\text{H}$ compounds.



Pyrolysis of 2-phenylethylboranes gives boraindanes having not only aralkyl groups on the boron but also alkaryl groups, e.g., *o*-ethylphenyl groups (LVIIb); this arises from dehydrogenation-hydrogenation by the following scheme:



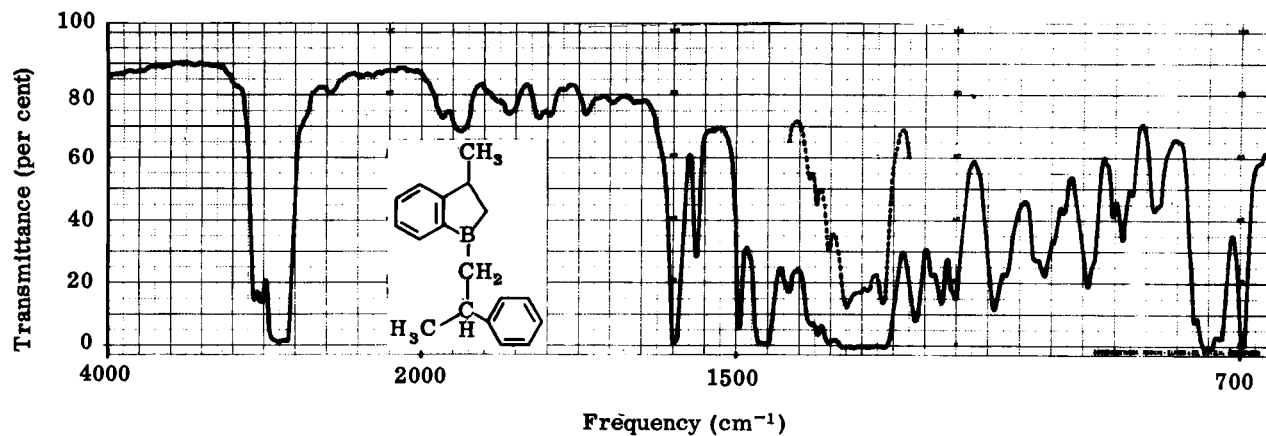


FIG. 8. Infrared spectrum of B(2'-phenylpropyl)-3-methylboraindane, (LVI). Solid line: $d = 0.05$ mm (NaCl prism); dashed line, ca. 10 % cyclohexane solution.

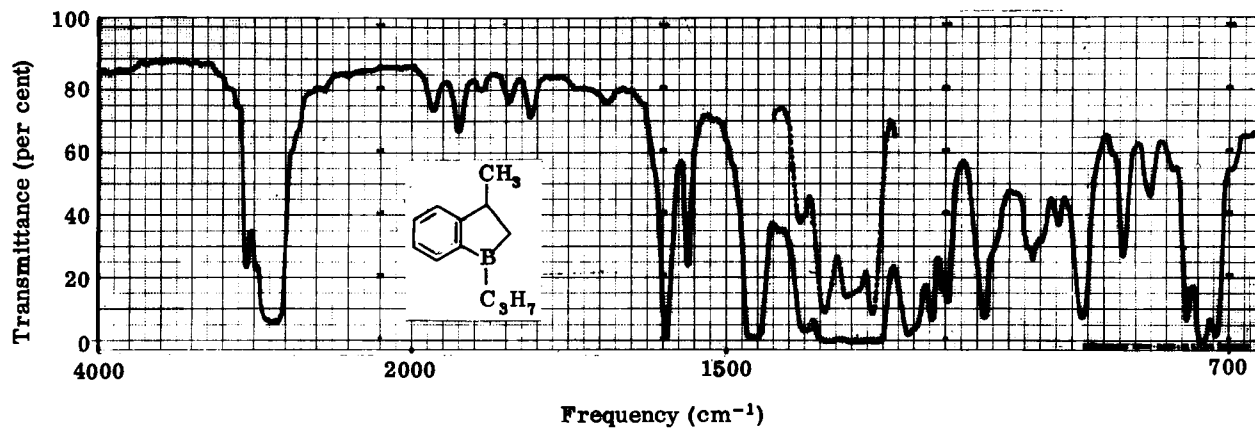
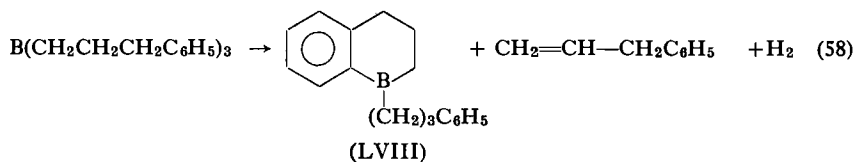
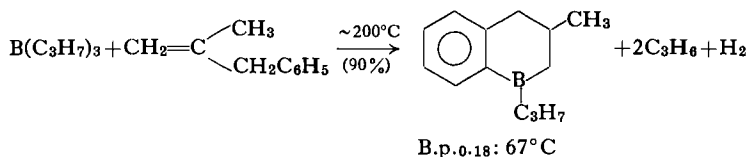


FIG. 9. Infrared spectrum of B-propyl-3-methylboraindane. Solid line: $d = 0.05$ mm (NaCl prism); dashed line, ca. 15% cyclohexane solution.

Boratetralins can be prepared in the same way. Tri(3'-phenylpropyl)-borane loses allylbenzene and H_2 at $200^\circ C$ to give B-(3'-phenylpropyl)-boratetralin (LVIII).

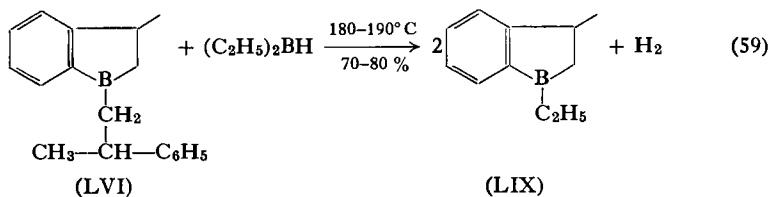


1-Propyl-3-methylboratetralin can be prepared in an analogous way (83).

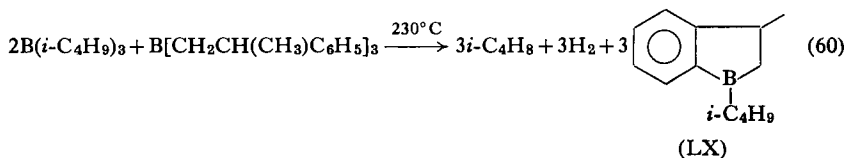


These boron heterocyclics will always be formed under pyrolytic conditions, whenever at least one boron-attached aralkyl group which can form a five- or six-membered ring is present. The other two boron substituents may be the same or different, but one of them must be hydrogen or a group that can form a B—H bond through dehydroboration (e.g., a B—C_{alkyl} group containing more than two carbons); the third group may be quite different. It determines the boron-bonded group outside of the ring (71).

1-Aralkylboraindanes and 1-aralkylboratetralins convert readily to the 1-alkyl derivatives (69). If an alkylidiborane or R_3NBH_3 is added dropwise to 1-aralkyl compounds at $180\text{--}190^\circ C$, hydrogen is evolved and 1-alkyl compounds (e.g., LIX) are formed in 70–80 % yield.

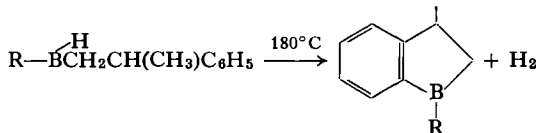
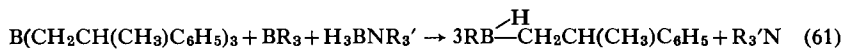


Dialkyl monoaralkylboranes or a mixture of trialkyl- and triarylboranes may also be used to prepare boraindanes and boratetralins (68, 69). Two moles of $(i\text{-Bu})_3B$ and one mole of tri(2-phenylpropyl)borane form 1-isobutyl-3-methylboraindane (LX) in over 90 % yield at $230^\circ C$.

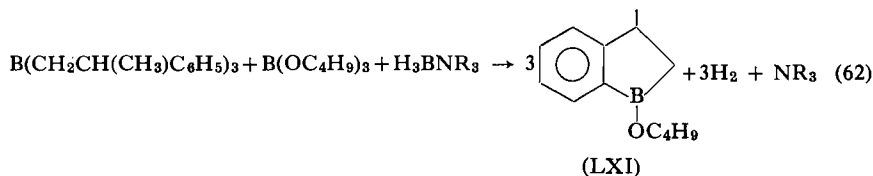


Since the olefin formed is very volatile, the reaction may be done at atmospheric pressure.

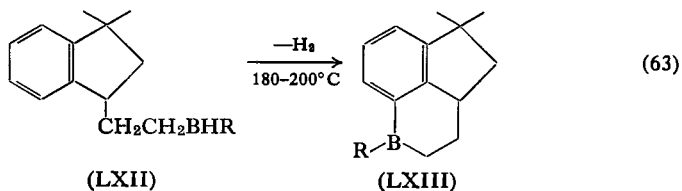
Aralkyldiboranes lose hydrogen about 150°C to form 1-boraindanes and 1-boratetralins. Because of the high borohydride concentration, side reactions cannot be avoided, and the reaction mixture becomes colored, yielding polymeric products. The borohydrides must be stabilized by addition of Lewis bases, such as trialkylamines. Trialkylamine-boranes which are simple to measure and easy to handle can be used as sources of boron hydrides in pyrolysis. Aminoboranes are not formed if the high-temperature reaction time is not too long. A mixture of equimolar quantities of triaralkylborane, trialkylborane, and trialkylamine-borane undergoes substituent exchange on boron, like the intermediate aralkylalkylborane, and forms 1-alkylboraindane or 1-alkylboratetralin (68).



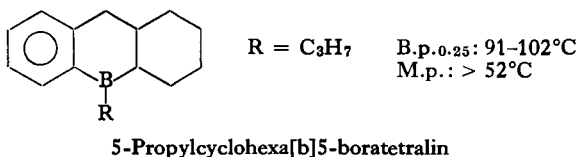
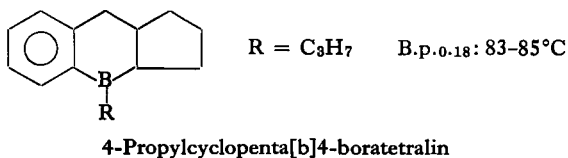
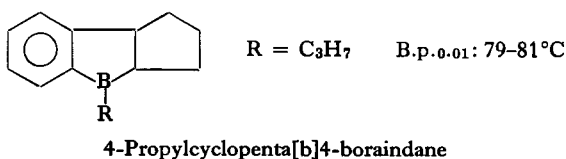
Trialkylboranes can also be replaced by esters of orthoboric acid (tri-alkoxyboranes). An equimolar mixture of R_3B , R_3NBH_3 , and $\text{B}(\text{OR}_3')$ yields B-alkoxy-1-boraindanes; in this manner, B-butoxy-3-methylboraindane (LXI) was obtained in 85 % yield at 190°C (71).



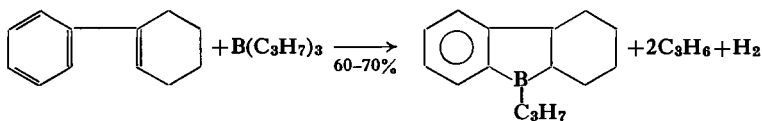
Other boron heterocyclics may be prepared in similar fashion. A mixture of tri- $[\beta\text{-(3',3'-dimethylindanyl)ethyl}]$ borane (LXII) and $(\text{C}_2\text{H}_5)_3\text{N}\cdot\text{BH}_3$ in the presence of $(i\text{-C}_4\text{H}_9)_3\text{B}$ yields tricyclic (LXIII).



In addition to these compounds the following boronheterocyclics are obtained in high yields (85–95%) (83).

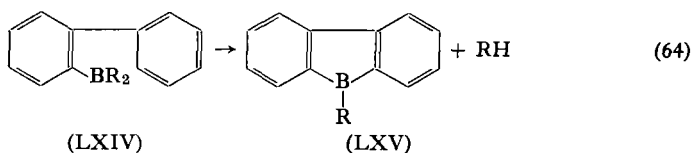


5-Propylhexa[b]5-boraindane is obtained (60–70%) from tripropylborane and cyclohexenylbenzene through displacement and dehydrogenation reactions (83).



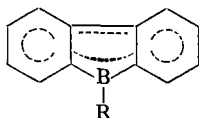
5. 9-Borafluorenes

2-Biphenylyldialkylboranes (LXIV), prepared from 2-lithiobiphenyl and R₂BCl, split out a hydrocarbon molecule when heated to 180–200°C to give 9-alkylborafluorenes (LXV) (65% yield for R = C₂H₅).



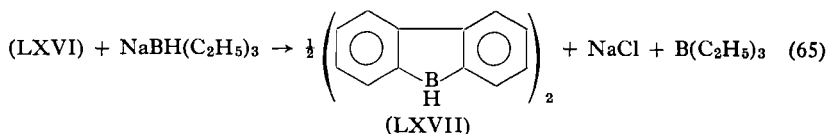
If R is a higher alkyl group, such as propyl or isobutyl, dehydroboration with B—H formation can occur and H₂ splits off. In this case a cleavage of biphenyl is also possible. Consequently, yields of 9-propylborafluorene (42 %) and 9-isobutylborafluorene (40 %) are lower than for the ethyl analog. 2-Biphenylyldiphenylborane splits out benzene at 280–300° C, forming 9-phenylborafluorene in 55 % yield.

9-Borafluorenes (44) having alkyl or aryl substituents are *intensely yellow*. This is evidently due to a degeneration of the aromatic system through the boron, so that a large part of the compound exists in the resonance form.

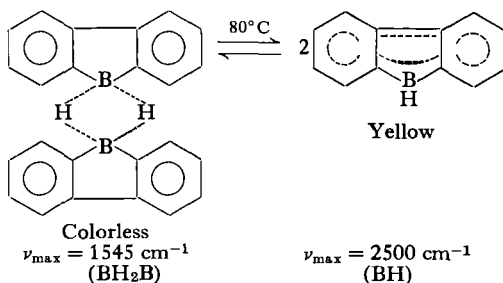


Reaction of 9-alkyl or 9-arylborfluorenes with BCl₃ in the presence of borohydrides (12) gives the yellow 9-chloroborfluorene (LXVI); this forms a colorless diethyl etherate which dissociates at its melting point (82° C).

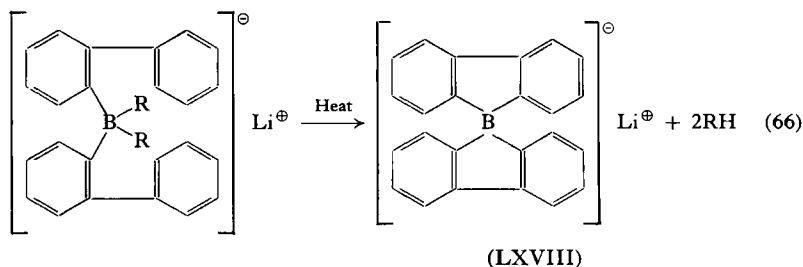
(LXVI) reacts with NaBH(C₂H₅)₃ in a 1:1 ratio in hexane to give the colorless, slightly soluble bis(9-borfluorene) (LXVII).



(LXVII) heated in benzene, undergoes reversible dissociation at 80° C to form the yellow 9-borfluorene.



A 2:1 ratio of 2-lithiobiphenyl and diaryl or dialkylchloroborane, when pyrolyzed, gives lithium bis(2,2'-biphenyl)spiroboranate (LXVIII) (43).



The properties of the 9-borafluorenes are summarized in Table III.

TABLE III
9-BORAFLUORENES

Compound	B.p. (°C/mm)	M.p. (°C)	Color	Max. ab. (cm ⁻¹)
9-Ethylborafluorene	112°/0.3	16°	Yellow	15,800
9-Propylborafluorenes ^a	130°/0.2	5°	Yellow	—
9-Isobutylborafluorene	160°/0.2	13.5°	Yellow	—
9-Phenylborafluorene	180°/0.4	118°	Yellow	24,700
Bis(9-borafluorene)	—	107°	Colorless	—
9-Chloroborafluorene	110°/0.1	52°	Yellow	25,200

^a Mixture of 1-propyl and 2-propyl compounds.

IV

PROPERTIES AND REACTIONS OF HETEROCYCLIC ORGANOBORANES WITH ONE BORON ATOM

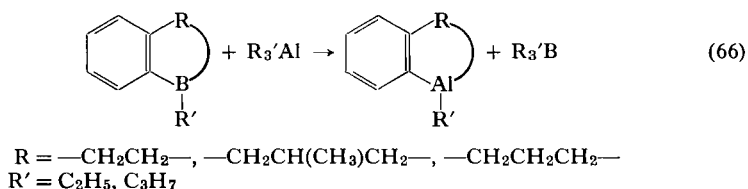
A. Summary of Typical Organoboron Heterocyclics

Some of the basic types of heterocyclic organoboranes are presented in Table IV (pages 298 and 299).

B. Special Reactions of Heterocyclic Organoboranes

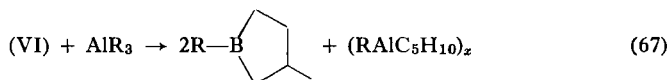
1. Reaction with Organometallic Compounds

Exchange reactions between boron and aluminum alkyls (9, 72) may be used to prepare five- and six-membered organoaluminum heterocyclics (72-74). In the reaction of one mole of B-ethylboraindane or boratetralin (68) with one to one and one-half of moles Et_3Al heated to 100°C , Et_3B may be removed under reduced pressure, leaving the well-crystallized 1-ethylaluminaindanes or aluminatetralins (72).

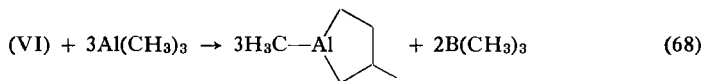


In contrast to their boron analogs, the aluminaindanes and tetralins (Table V) are dimeric in cyclohexane or benzene solutions; however, they will form monomeric complexes with ether or pyridine (the pyridine complex of 1-propyl-3-methylaluminaindane melts at 93.5°C).

Alkyl exchange between bis(borolanyl)alkanes (VI) (23, 27) and aluminum alkyls in a 1:1 ratio gives B-alkylborolanes and organoaluminum polymers (27).



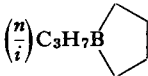
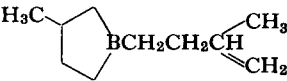
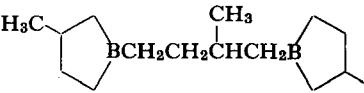
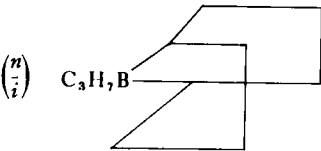
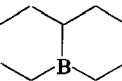
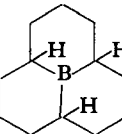
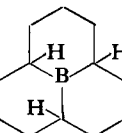
However, if the aluminum alkyls are present in excess (e.g., 3:1 or 4:1), 1-alkylaluminacyclopentane (distillable under high vacuum) forms (72).



The colorless liquid aluminum compound is dimeric in cyclohexane; at 100°C , it decomposes into a glassy polymer.

Diethylmagnesium and B-alkylboraindane react via a partially isolable intermediate (LXIX) to form crystalline spiro complexes (LXX) (75).

TABLE IV
PHYSICAL PROPERTIES OF VARIOUS HETEROCYCLIC ORGANOBORANES

Compound	Formula	B.p. (°C/Torr)	M.p. (°C)	d_4^t	n_D^t
1-Propylborolanes (Isomeric mixture)	$\left(\begin{smallmatrix} n \\ i \end{smallmatrix}\right) C_3H_7B$ 	64–66°/100	—	0.7876 ₂ ²⁰	1.4478 ₇ ²⁰
1-Isopentenyl-3-methylborolane		67–68°/9	—	0.7929 ₃ ²⁰	1.4525 ₇ ²⁰
Bis-1,4(3'-methylboracyclopentyl)-2-methylbutane		86°/0.2	—	0.8256 ₅ ²⁰	1.4599 ₈ ²⁰
9-Propyl-9-borabicyclo[3.3.1]nonanes (Isomeric mixture)	$\left(\begin{smallmatrix} n \\ i \end{smallmatrix}\right) C_9H_7B$ 	94–95°/14	—	0.8688 ₂ ²⁰	1.4707 ₀ ²⁰
9-Boradecalin		102–103°/100	—	0.8684 ₉ ²⁰	1.4792 ₀ ²⁰
<i>cis,cis,cis</i> -Perhydro-9b-boraphenalene		115°/10	—	0.9357 ₁ ³⁵	1.5100 ³⁵
<i>cis,cis,trans</i> -Perhydro-9b-boraphenalene		113.5°/10	31°	0.9220 ³⁵	1.5029 ³⁵

13-Boratricyclo[6.4.1.0 ^{4,13}]tridecane		113.0°/10	—	0.9219 ³⁵	1.5058 ³⁵
1-Ethyl-3-methylboraindane		99–100°/15	—	—	1.5231 ₄ ²⁰
1-Propyl-3-methyl-1-boraindane (Isomeric mixture)		92–94°/8	—	0.9001 ₅ ²⁰	1.5139 ₂ ²⁰
1(2'-Phenylpropyl)-3-methyl-1-boraindane		122°/0.4	—	0.9787 ₇ ²⁰	1.5650 ²⁰
2'-Phenylethyl-1-boraindane		99–102°/0.05	49°	—	1.5240 ₁ ⁵⁰

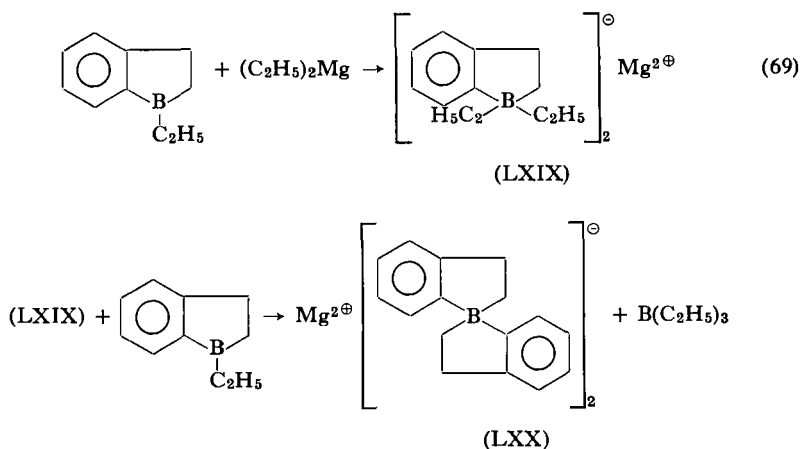
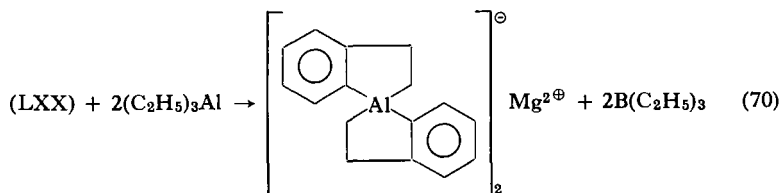


TABLE V

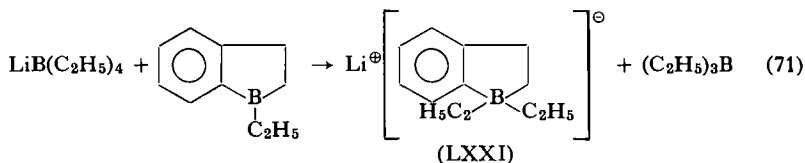
1-ALKYLALUMINAINDANES AND ALUMINATETRALINS

Compound	M.p. (°C)
1-Propylaluminaindane	52°
1-Ethyl-3-methylaluminaindane	102°
1-Propyl-3-methylaluminaindane	103°
1-Propylaluminatetralin	Liquid

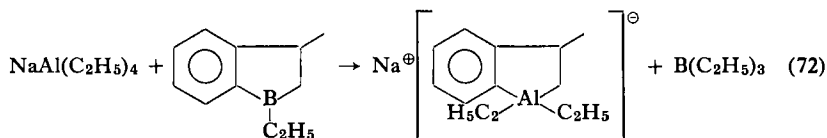
These complex salts are appreciably soluble in aromatic hydrocarbons, but only slightly soluble in aliphatic hydrocarbons. Reaction of (LXX) with triethylaluminum causes replacement of the boron (75).



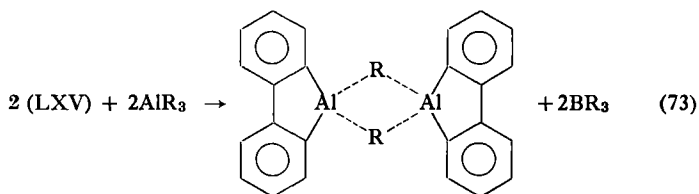
Substitution of $\text{LiB}(\text{C}_2\text{H}_5)_4$ for $\text{Mg}(\text{C}_2\text{H}_5)_2$ does not give the spiro anion (LXX) but only the addition compound (LXXI).



Excess boraindane may be removed by distillation. The reaction between boraindanes and $\text{NaAl}(\text{C}_2\text{H}_5)_4$ is similar, except that it is the complex of the aluminaindane that is isolated.

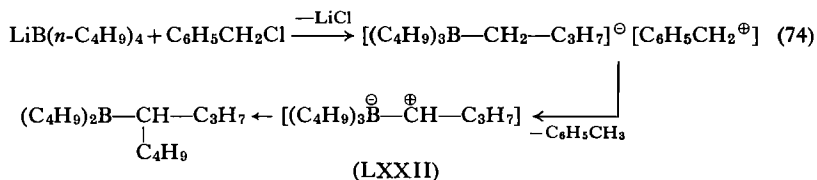


9-Alkyl- or 9-arylborafluorenes (LXV) react with $(\text{C}_2\text{H}_5)_3\text{Al}$ to give alkyl (or aryl) exchange (72), triethylborane is formed along with the colorless dimer of the 9-alkyl- or arylaluminafluorene (72, 73). Deuterolysis of this compound gives monodeuterobenzene and 2,2'-dideuterobiphenyl (72).

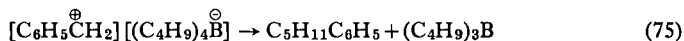


2. Reaction with Alkylating Agents—Ring Expansion of Boron Heterocyclics

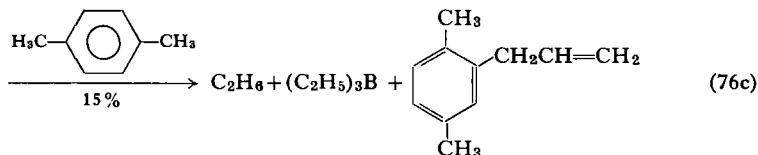
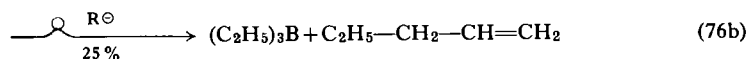
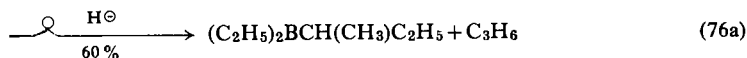
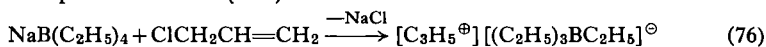
NaBR_4 reacts with alkylating agents, such as $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (76), allyl chloride (77), and triethyloxonium tetrafluoroborate (76, 77), to undergo a type of solvent-dependent ion-pair reaction yielding various organo-boranes (76, 77). For example, $\text{LiB}(n\text{-C}_4\text{H}_9)_4$ reacts with $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ in ether, giving, among other products, di-butyl-4-octylborane; the mechanism involves formation of an unstable "boron-ylid" (LXXII) followed by anionic rearrangement (76).



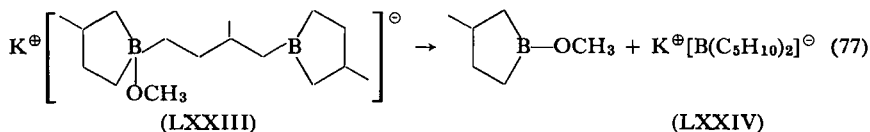
Another way that the "benzylum-tetraalkylboranate" ion pair can stabilize itself is by alkyl migration from boron to carbon, yielding 1-pentylbenzene and tri-1-butylborane (76).



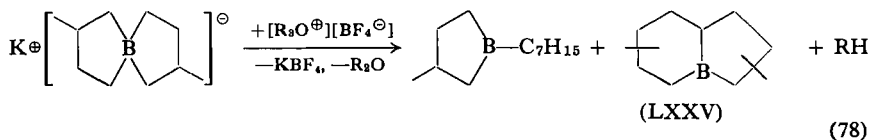
$\text{NaB}(\text{C}_2\text{H}_5)_4$ reacts with allyl chloride in *p*-xylene to give diethyl-2-butylborane, triethylborane, propylene, and 1-pentene (77). The *p*-xylene can also react to split off ethane (76c).



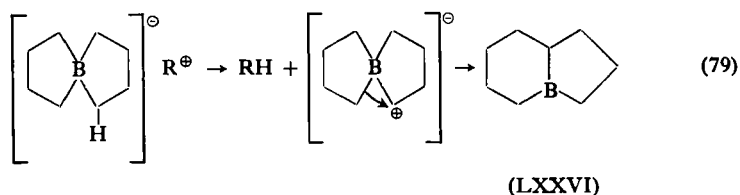
Tetraalkylboranates having bifunctional organic groups [e.g., spiroboranates with two alkylene groups] also react with alkylating agents. Various ring compounds may be formed, or hydride migration may occur via a "boron-ylid"), forming new boron heterocyclics. For example, potassium bis(3-methylbutylene)boranate (LXXIV) [made from bis(3'-methylborolanyl)-2-methylbutane (LXXIII) and KOCH_3 (77), reacts



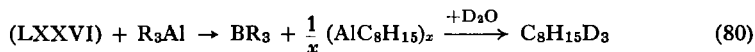
readily with $(\text{C}_2\text{H}_5)_3\text{OBF}_4$ to form two isomeric isopentylborolanes and four isomeric dimethylborahydrindanes (LXXV) which may be separated by gas chromatography.



Alkylation in the preceding example proceeds by splitting off ethane and stabilization of the "boron-ylid" intermediate by ring expansion.

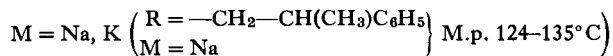
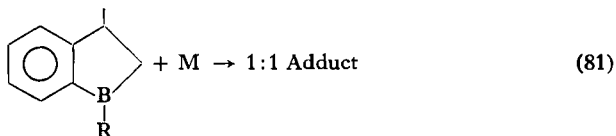


The trifunctional group of borahydrindanes may be converted to tri-deuteroalkanes by reaction with aluminum alkyls (9), followed by deuterolysis.

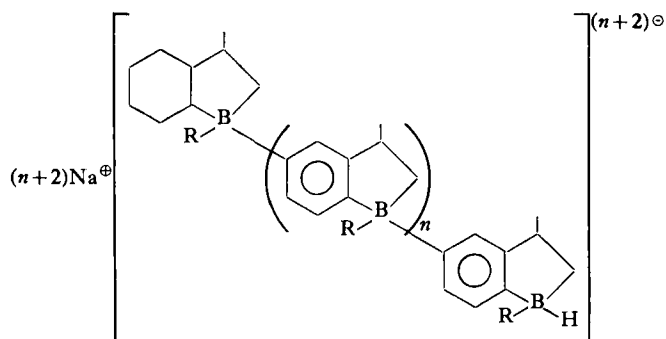


3. Reaction of Boraindanes with Alkali Metals

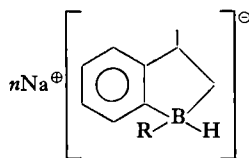
B-alkyl and B-aralkylboraindanes (68) react with sodium or potassium to form colorless, crystalline solids, more or less soluble in aromatic hydrocarbons, having a 1:1 metal-boraindane ratio (78). They resemble the compounds of Na with $(\text{C}_6\text{H}_5)_3\text{B}$ and $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{B}$ (79), also colorless materials.



Warming a benzene solution of B-alkyl or B-arylboraindanes in the presence of metallic sodium (present as strips or amalgam) produces a colored solution, whose ESR spectrum indicates a free radical. Gradually a colorless, diamagnetic solid separates out. Molecular weight determinations (melting point depression in benzene) indicate a pentameric or hexameric species. The compound appears to be a complex salt, having four-coordinated boron, of the structures LXXVII and LXXVIII.



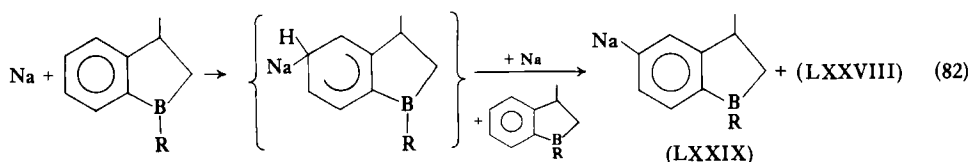
(LXXVII)



(LXXVIII)

The observed color changes during salt formation are due to the various reaction intermediates. One possible first reaction step is the nucleophilic substitution of an alkali metal on the phenyl group. Direct interaction between sodium and boron, previously hypothesized, seems rather unlikely.

The next intermediate, (LXXIX), forms high molecular weight salts containing four-coordinated boron.

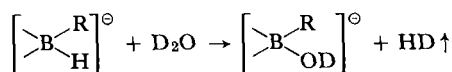


Structures (LXXVII) and (LXXVIII) were determined by experimental work; each has a B—H band.

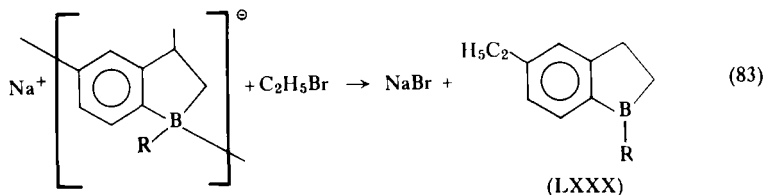
Other complex salts have bands around 1850 cm^{-1} : $\text{NaBH}(\text{C}_3\text{H}_7)_3$ appears at 1830 cm^{-1} (77); B-2'-phenylpropyl-3-methylboraindane (m.p. 186°C) has a broad band at $1850\text{--}2200\text{ cm}^{-1}$ with maxima at 1950 and 1970; R_3B and NaH compounds have a band at 1850 (80), while Na and $(\text{C}_6\text{H}_5)_3\text{B}$ or $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{B}$ have a broad band at 1970 cm^{-1} . (LXXVII) and (LXXVIII) show broad B—H bands between 1850 and 2200 cm^{-1} , with maxima at 1950 and 1970.

Other evidences for the presence of the B—H group are:

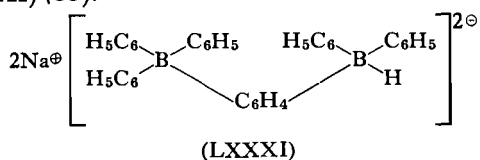
- (1) Reaction with ethylene at 150° C gives B-alkyl compounds, alcoholysis of which does not evolve H₂.
- (2) Deuterolysis gives primarily hydrogen deuteride.



Reaction of the sodium boraindane compound with C₂H₅Br in benzene at room temperature yields NaBr and a nonsaltlike compound, whose infrared spectrum indicates the presence of the boraindane group and a 1,2,4-trisubstituted phenyl ring (band at 821 cm⁻¹) (LXXX).

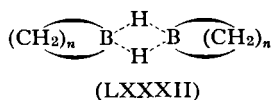


Since the boraindane sodium “adduct” is very similar in its properties and reaction products to the “addition compound” of (C₆H₅)₃B and sodium (79), the structures are analogous (78). The Na-(C₆H₅)₃B compound may be a complex salt having four-coordinated boron, having the following structure (LXXXI) (88).

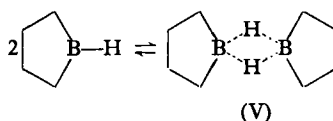


C. Bis(boracyclanes)

Bis(boracyclanes) (LXXXII) (10) vary in stability depending on the type of carbon bonded to the boron (e.g., primary, secondary); ring size also plays a very important part. The equilibrium between monomer and dimer



at room temperature for five-membered rings (borolanes) lies completely on the side of the dimer.



The B—H bonds of (V) react with water to give off hydrogen only above 100° C; likewise, addition to olefins only occurs at elevated temperatures. Under ordinary conditions, the boron-carbon bonds of bis(borolanes) are

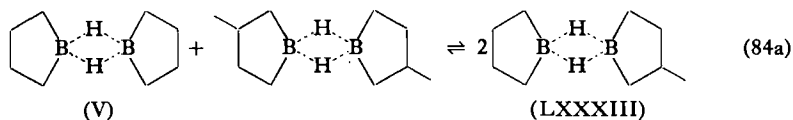
TABLE VI
BIS(BOROLANES)

Compound	B.p. (°C/mm)	M.p. (°C)	n_D^{20}	d_4^{20}
Bis(borolane)	76–77/10	—	1.4894 ²⁰	0.8541
Bis(3-methylborolanes) ^a	95/12	—	1.4762 ²⁰	0.8307
Bis(3,4-dimethylborolanes) ^a	120–124/12	~ 30	1.4683 ²⁵	—

^a Mixture of isomers.

stable to oxidation by many media, and do not undergo autoxidation. H₂O₂ cleaves the bonds only slowly. (V) and bis(3-methylborolane) do not react with CH₂N₂ at room temperature; the failure to observe the catalytic decomposition to N₂ and “polymethylene” indicates that the borolane boron is exclusively four-coordinated. Bis(borolanes) also do not catalyze substituent exchange on boron (8, 9, 12); only above 100° C do they act like open-chain alkylidiboranes.

A mixture of (V) and bis(3-methylborolane) heated to 120–140° C slowly yields borolane-3-methylborolane (LXXXIII)



The reaction is easily followed by gas chromatography (Fig. 10) or mass spectroscopy (6).

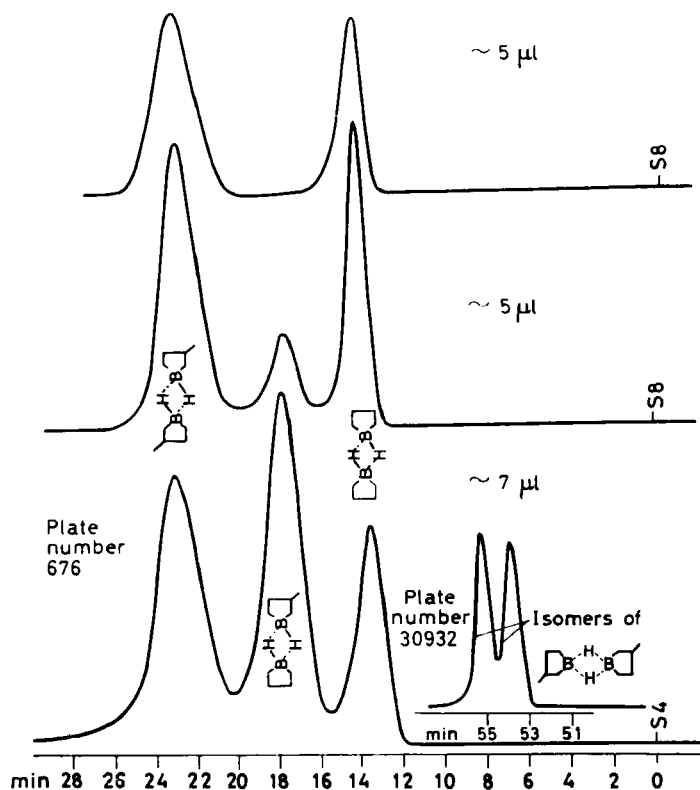
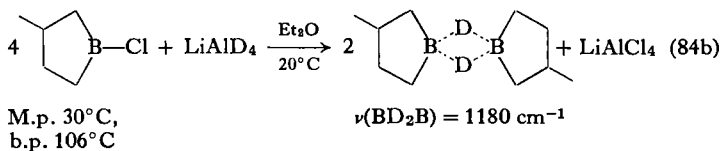


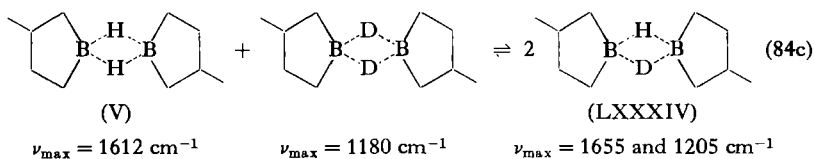
FIG. 10. Dissociation-association equilibria of bis(borolanes).

	Main figure	Small figure
Stationary phase:	silicone oil DC 710	methyl silicone rubber SE 30
Carrier gas:	helium, 105 ml/min	argon
Inlet pressure:	0.5 atg	0.7 atg
Column:	1 meter	40 meter \times 0.25 mm i.d.
Temperature:	116°C	105°C
Sample size:	5.5 and 7 μ l	1 γ

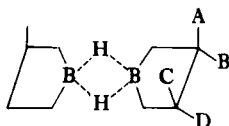
Mixtures of bis(borolanes) and bis(B-deutero borolanes) (easily-formed from B-chloroborolanes and LiAlD_4) (20), give a similar reaction which can



be followed by infrared spectroscopy (Fig. 11). The product (LXXXIV) has two new bands due to the bridging group (81).

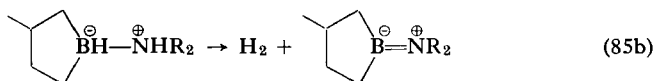
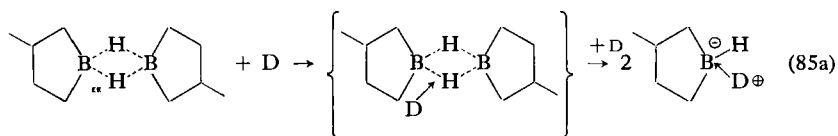


Bis(3-methylborolane) can have four different isomers, two of which can be separated by gas chromatography (6).

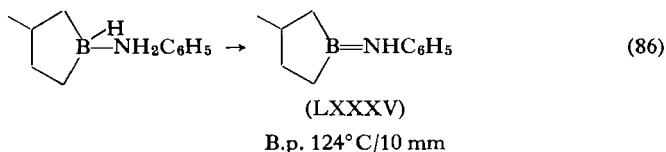


Similarly, bis(3,4-dimethylborolane) should have three different forms, two of which, because of strong bridge bonds, will have two different stereoisomers each.

Stable bis(borolanes) react very rapidly at room temperature with compounds having strong donating groups. Amines, such as pyridine, benzylamine, and even ammonia, add readily to borolanes at 0° C, eliminating the electron-deficient bonds (85a). If the amine has a hydrogen on it, H₂ is eliminated (85b) to form aminoborolanes (82).



The weaker base aniline splits bis(3-methylborolane) at about 40° C to form 3-methylboracyclopentylaniline (LXXXV) (82).



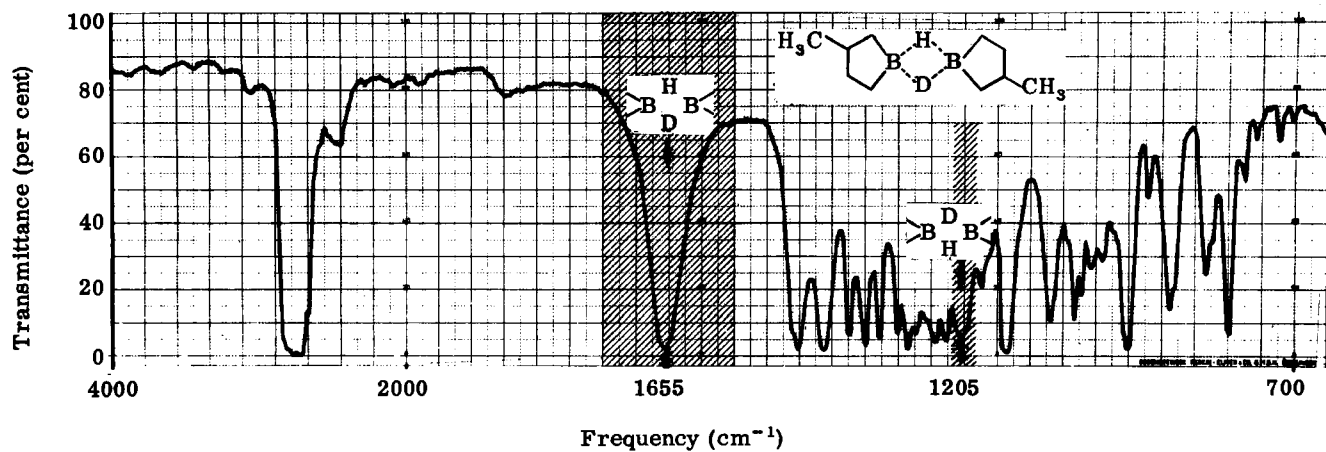
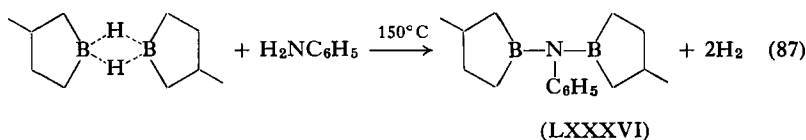


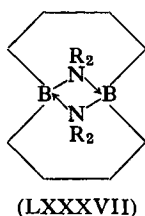
FIG. 11. Infrared spectrum of bis(3-methylborolane) from 3-methylborolane and B-deutero-3-methylborolane; $d = 0.05$ mm (NaCl prism). Neat, except for the darkened areas, which were run in ca. 15% solution.

At higher temperatures (about 150° C), primary amines react with a mole of bis(borolane) to split off two moles of H₂.

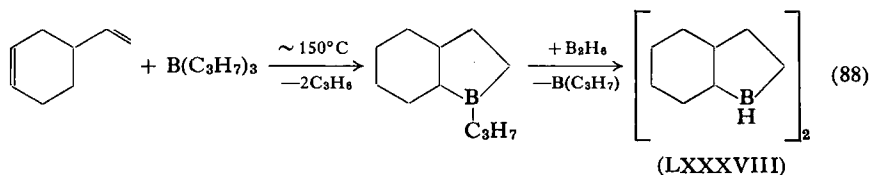


Similar products one obtains with C₆H₅CH₂NH₂ and C₂H₅NH₂. Tetra-alkyldiboranes R₄B₂H₂ react with amines to give different types of products (82).

The aminolysis products of bis(borolanes) under mild temperature conditions indicate that their surprising stability is due to the five-membered ring structure. A bis(1,2-tetramethylene)diborane (50) should form an aminoborane having structure (LXXXVIII), but this is not the case.



The particular stability of five-membered rings is apparently limited to simple bis(borolanes) having two B—C_{prim} linkages. Bis(1-borahydrindane) (LXXVIII) [ν_{max} (BH₂B) = 1565 cm⁻¹] reacts like an open-chain alkyl-diborane (83).



The dimerization energy of (LXXXVIII) is low in comparison to other bis(borolanes), apparently because the boron is bonded to a secondary carbon. Five-membered boron heterocyclics with B—H bonds, whose boron is attached to an aromatic ring, react as readily as open-chain alkyl or aryl-diboranes at room temperature (68). The dimerization tendency of borahydrindane (LXXXIX) (68), boratetralin (XC) (68), and 9-borafluorene (XCI)

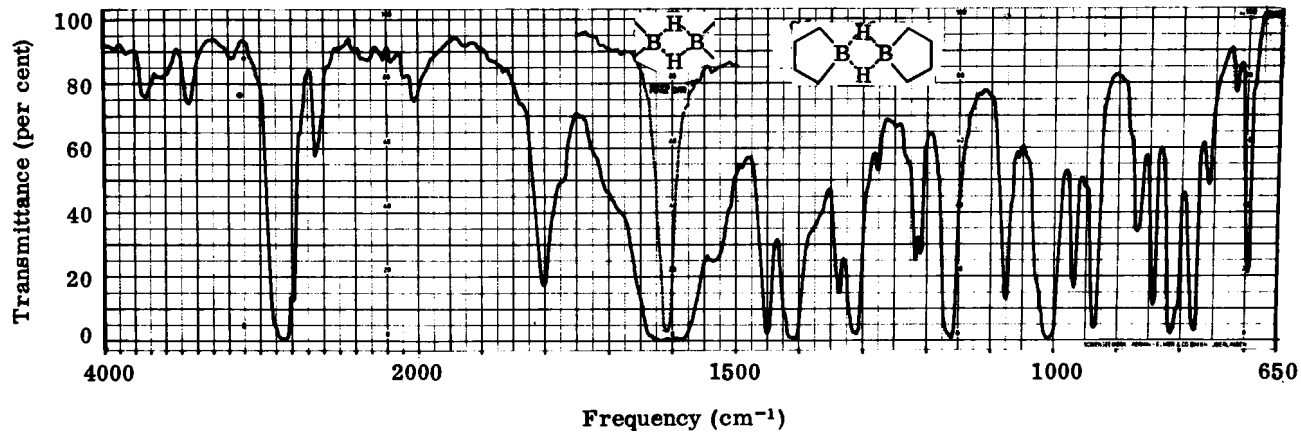
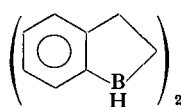


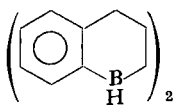
FIG. 12. Infrared spectrum of bis(borolane). Solid line $d=0.05$ mm (NaCl prism); dashed line: ca. 4% cyclohexane solution.

(44) is markedly less than that of simple borolanes, because of the interaction of the boron with the aromatic rings.



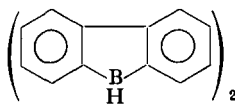
(LXXXIX)

M.p. 132° C



(XC)

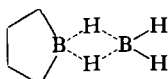
M.p. 103–104° C



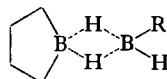
(XCI)

M.p. 107° C

The gradual change in reactivity between borolanes and boraindanes or similar compounds may be qualitatively determined by the position of the infrared absorption of the BH_2B bridge. While this has a maximum of 1612 cm^{-1} (see Fig. 12) in bis(borolanes), it drops to 1545 cm^{-1} in boraindanes, appreciably lower than the figure of 1565 cm^{-1} for tetra-1-alkyldiboranes. Also, the mixed dimers (XCII) and (XCIII) are less stable to oxidation and hydrolysis than bis(borolanes) (81, 82), this is in agreement with the BH_2B band appearing at 1567 cm^{-1} .

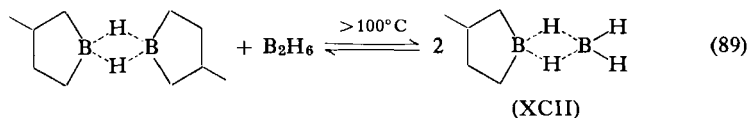


(XCII)

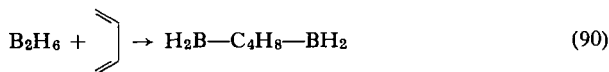


(XCIII)

(XCII) can be obtained from diborane and bis(borolane).



The mixed diborane (XCII) formed at a high-temperature equilibrium may be distilled off at room temperature under reduced pressure. The infrared spectra of (XCII) (Fig. 13) and of the 3-methyl derivative (broad BH_2 band at 2500 cm^{-1}) enable the determination of 1,2-tetramethyldiborane (XCIV) (84). This compound can be made by bishydroboration of butadiene or isoprene with B_2H_6 at low temperature (84).



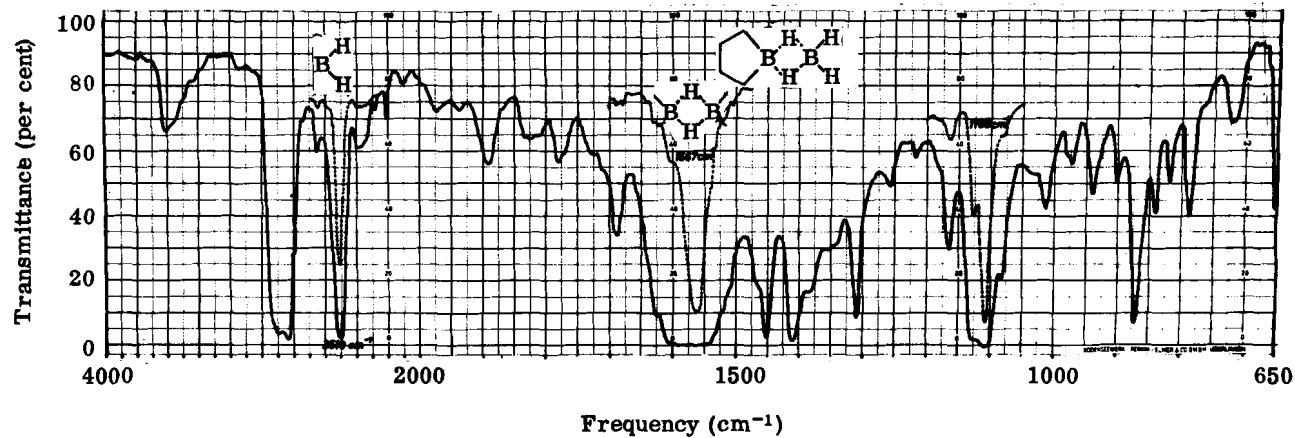
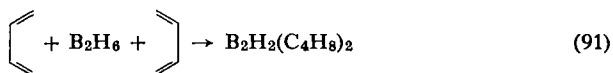


FIG. 13. Infrared spectrum of borolaneborane (XCII). Solid line: $d = 0.05$ mm (NaCl prism); dashed line: ca. 5% cyclohexane solution.

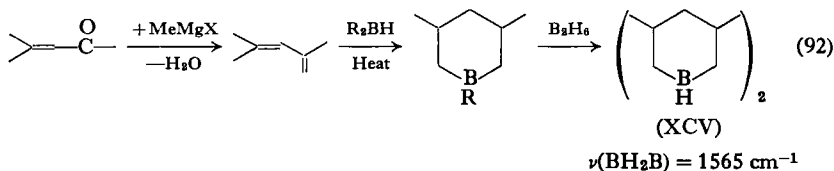
The B^{11} NMR is consistent with the following symmetric structure (84).



At elevated temperatures, the "symmetric" and "asymmetric" forms are in equilibrium with each other. Bis(borolane) (V) may be prepared in the same fashion; alkyldiboranes formed at room temperature from B_2H_6 and butadiene will isomerize into (V), due to the latter's great stability (82).

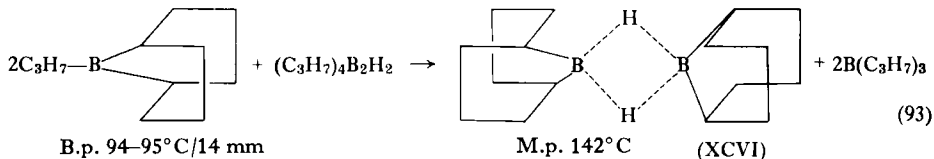


Pure bis(borinanes) must be prepared at temperatures below 100°C ; otherwise, they isomerize into the five-membered ring structure. Ring contraction in 3,5-dimethylborinane (XCV) (51), prepared in the following fashion, is practically avoided, since it would involve attachment of the boron to a tertiary carbon.



(XCV) reacts readily, in the same fashion as an open-chain alkyldiborane (e.g., tetraethyldiborane), with various reagents at 0°C , such as water (B—H hydrolysis), olefins (hydroboration), and atmospheric oxygen (oxidation of B—H and B—C bonds).

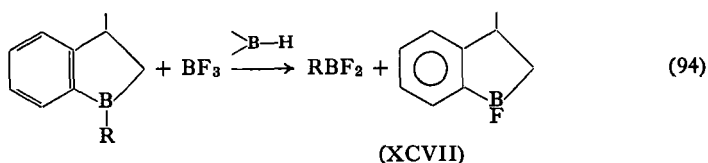
Another alkyldiborane having boron in a six-membered ring is the crystalline bis (9-borabicyclo[3.3.1]nonane) (XCVI), readily prepared from propyldiborane and B-propyl-9-borabicyclo[3.3.1]nonane (10).



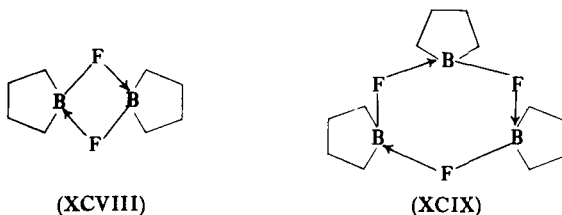
(XCVI) is apparently less stable than ordinary bis(borolanes), for it readily reacts with alcohol at 40° C, evolving hydrogen; this is due to the boron being in a six-membered ring and bound exclusively to secondary carbon atoms.

D. B-Halogenated Borolanes and Boraindanes

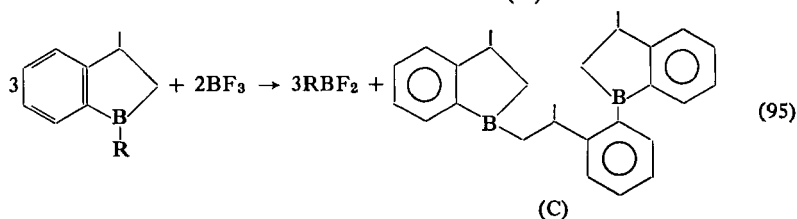
Reaction of B-alkylboraindanes or borolanes at 100–200° C with BF_3 (gas or as liquid etherate) in the presence of catalytic amounts of borohydrides produces B-fluoroboraindanes or borolanes (XCVII) (28).



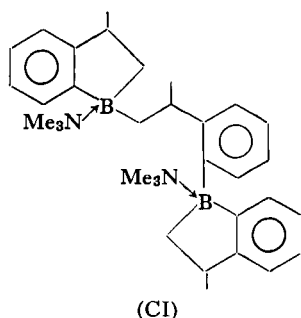
The alkyldifluoroboranes may readily be distilled out of the system. In contrast to the corresponding reaction with BCl_3 , pure B-fluoroborolanes or boraindanes are not obtained, because these compounds are associated either with each other or with BF_3 . The dimer (XCVIII) and trimer (XCIX) can be used to synthesize fluorine-rich or fluorine-free boron compounds.



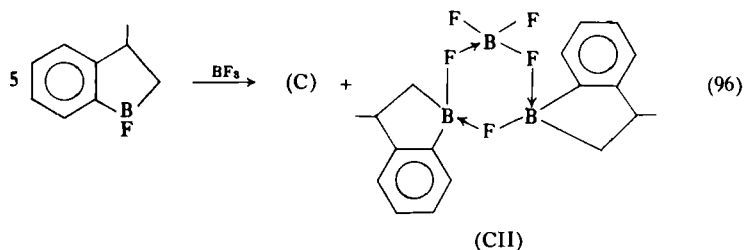
Three moles of B-alkylboraindane react with two moles BF_3 to give an alkyldifluoroborane and a fluorine-free substance (C).



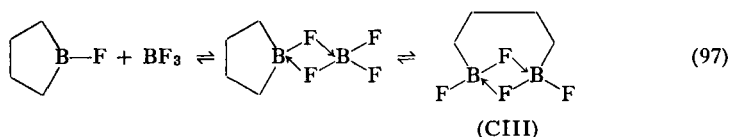
(C) forms a nicely crystalline bis(trimethyl)aminatate (CI).



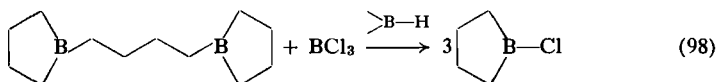
BF_3 reacts with an equimolar amount of B-alkylboraindane to form 1-fluoroboraindane, which forms a complex with excess BF_3 .



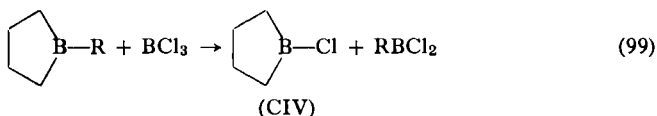
Excess BF_3 also reacts with borolanes or B-alkylboraindanes to give further expansion, yielding products of the type (CIII).



B-chloroborolane (CIV) is obtained in 90% yield from bis(borolanyl)-alkanes (27) and BCl_3 in a 1:1 ratio by heating with borohydrides [such as bis(borolane)] at 120–140°C (4b).

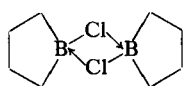


B-chloro heterocyclics (CIV) may also be prepared in good yields from BCl_3 and B-alkylborolanes.

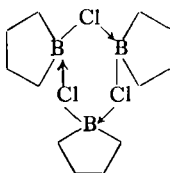


B-chloroboraindane (81) and 9-chloroboraffluorene (44) may be obtained in the same way.

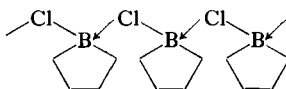
B-chloroborolanes (CIV) may be distilled at atmospheric pressure without decomposition (bath temperature about 200° C). While B-chloroborolane (b.p. 96–100° C) crystallizes after distillation, B-chloro-3-methylborolane (b.p. 110–112° C) may be gotten solid only by rapid cooling of the distillate at –40° C. The very mobile liquid slowly becomes highly viscous at room temperature, forming polymeric ring (CV, CVI) and chain (CVII) structures, which may be depolymerized by addition of B–H compounds and by heating.



(CV)



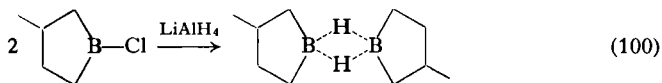
(CVI)



(CVII)

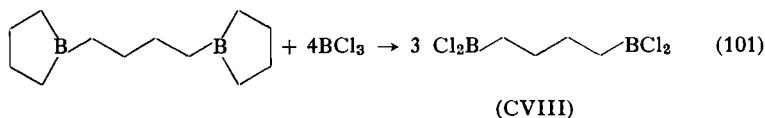
(CIV) is monomeric in dilute solutions of cyclohexane or benzene as determined by cryoscopic measurements (4b). 1-Chloroboraindane is also a volatile, mobile liquid at room temperature, and apparently lacks the ability to associate through chlorine bridges (72).

1-Chloroborolanes react with LiAlH_4 to form bis(borolanes) in high yields (72).



1-Chloroboraindanes form nicely crystalline dimeric boraindanes by an analogous reaction (81).

Reaction of bis(borolanyl)alkanes with excess BCl_3 cleaves the boron heterocyclic, forming bis(dichloroboryl)alkanes (CVIII) (28, 85).



V

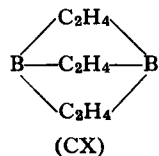
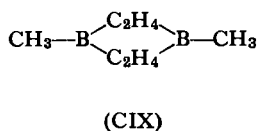
HETEROCYCLIC ORGANOBORANES WITH TWO OR MORE BORON ATOMS

Organoboron heterocyclics having more than one boron atom in the ring are still little known. In many cases, this type of compound is not especially stable at high temperatures, easily disproportionating after dehydroboration into polymeric products.

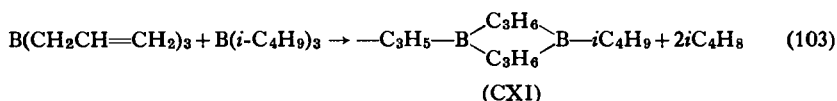
Treatment of B_2Cl_4 with ethylene gives 1,2-bis(dichloroboranyl)ethane (4a).



This, when treated with $(CH_3)_3B$ does *not* give compounds (CIX) and (CX) (86), but only polymers having the elements of (CIX).

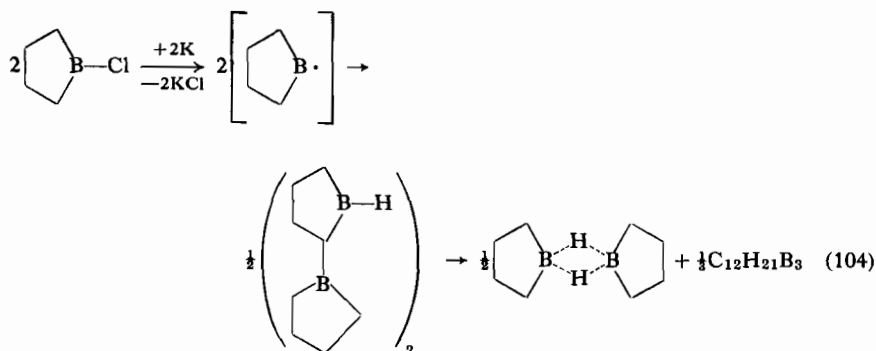


The product (CXI) of the displacement reaction between $B(i-C_4H_9)_3$ and $B(CH_2CH=CH_2)_3$ (59), on the basis of present knowledge about thermal isomerization of alkylboranes, cannot be solely the 1,5-diboracyclooctane derivative suggested. At high temperatures, it readily forms polymers and boron heterocyclics of other ring sizes.

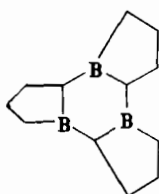


Another eight-membered ring, known for somewhat longer, is tetraboracyclooctane (XLVIII) (60), a pyrolysis product of $(CH_3)_3B$ (see Section IIID).

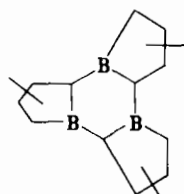
In exceptionally well-chosen cases, organoborane rings with more than one boron may be formed by disproportionation (4b). 2-Borolanylb borolane (formed from chloroborolanes and Na-K alloy at room temperature; BH_2B band at 1575 cm^{-1}), when heated to $60\text{--}70^\circ\text{C}$, yields bis(borolane) (BH_2B band at 1612 cm^{-1}) and a higher boiling product having three boron atoms in the molecule.



This higher boiling product has the formula $\text{C}_{12}\text{H}_{21}\text{B}_3$ (CVII), while the analogous product from 1-chloro-3-methylborolane has the formula $\text{C}_{15}\text{H}_{27}\text{B}_3$ (XX). Both are derivatives of 1,3,5-triboracyclohexane.

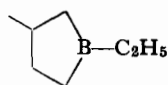


(CXII)

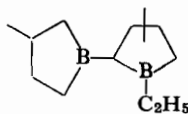


(XX)

If the intermediate borolane from 1-chloro-3-methylborolane is treated with ethylene at 120°C , two B-ethylated compounds are formed.



(CXIII)

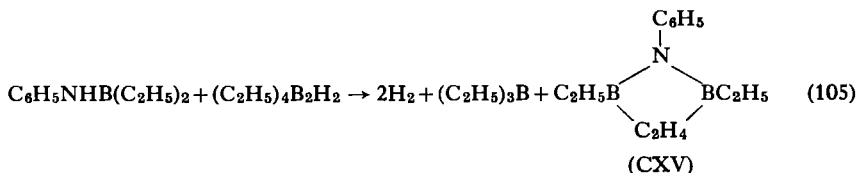


(CXIV)

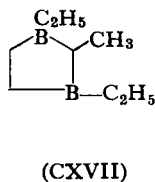
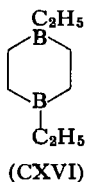
(CXIV) readily disproportionates in the presence of borohydrides (or by heating after dehydroboration) into (CXIII) and an isomer mixture of (XX) (4b).

Simple boron heterocyclics with two borons in the organic ring were recently reported (82, 87). If $\text{Et}_4\text{B}_2\text{H}_2$ is heated at 150°C with

$\text{C}_6\text{H}_5\text{NHB}(\text{C}_2\text{H}_5)_2$, hydrogen is given off and a compound (CXV) (b.p. $75^\circ\text{C}/0.3\text{ mm}$) having formula $\text{C}_{12}\text{H}_{19}\text{B}_2\text{N}$ is formed.



1,3-Diethyl-2-phenyl-1,3-dibora-2-azacyclopentane (CXV) reacts with triethylaluminum to undergo exchange of the boron-aluminum ligands, forming triethylborane and two higher boiling organoboranes, having molecular weights of 136 and 166 [bis(diethylboryl)ethane] and two boron atoms each. The 136 compound has the formula $\text{C}_8\text{H}_{18}\text{B}_2$; (CXVI) and (CXVII) are possible structures (87).



Homologous compounds can be synthesized from tetraethyldiborane and propyne (75). The compounds disproportionate, when heated, into $(\text{C}_2\text{H}_5)_3\text{B}$, and high molecular weight materials. Therefore (CXVI) and (CXVII) must be distilled at reduced pressure. (CXVI) and (CXVII) may also be prepared by the hydroboration of acetylene (90).



Polymeric materials may also be formed, moreover, a compound with the formula $\text{C}_{10}\text{H}_{21}\text{B}_3$ (CXVIII) is obtained with C_2H_2 (90). The mass spectrometer indicates a molecular weight of 174, and there are ten carbons and three borons per molecule.

(CXVIII) does not resemble simple boracyclanes in its high stability toward reactions with oxidizers (e.g., O_2 , H_2O_2). The retention time in a gas chromatograph is relatively short (see Fig. 14), indicating a spherical construction of the molecule. NMR (H^1 , B^{11}), infrared, and Raman spectra of (CXVIII) show that the compound is an organic derivative of the 2,3-carborane (89). Complete saturation of the three boron atoms in the C_2B_3

nucleus demonstrates similarity with aromatic hydrocarbons. (CXVIII) is the 1,5-dimethyl-2,3,4-triethyl-2,3-carborane with the following structure (90).

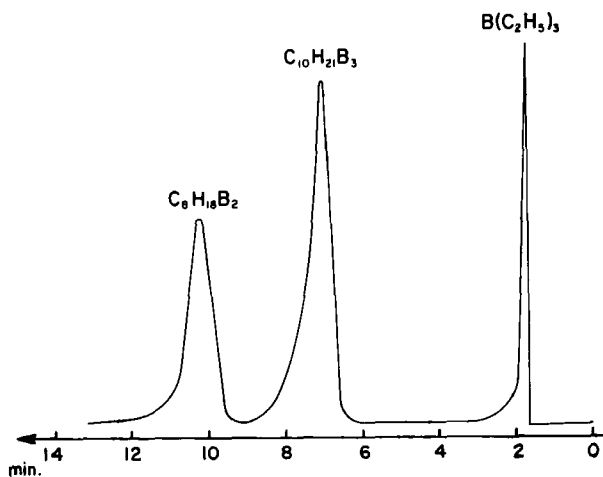
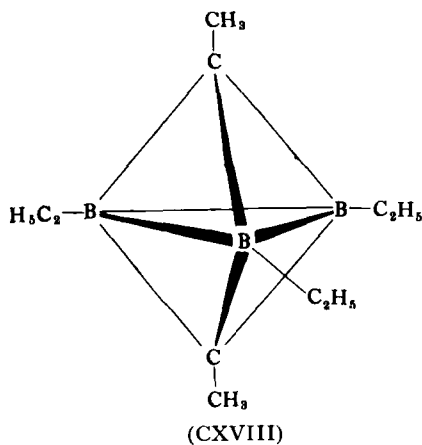


FIG. 14. Gas chromatographic separation of boron heterocyclics having several boron atoms in the ring. $C_8H_{18}B_2$ = (CXVI); $C_{10}H_{21}B_3$ = (CXVIII).

Column:	silicone oil DC 710 on Chromosorb 0.3–0.4 mm
Carrier gas:	helium, 78 ml/min
Temperature:	156° C
Inlet pressure:	0.5 atm
Sample size:	20 μ l

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Allyl Metal Complexes

M. L. H. GREEN and P. L. I. NAGY¹

*Inorganic Chemistry Laboratory,
University of Oxford,
Oxford, England*

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In this review the chemistry of allyl complexes of the transition metals is discussed, and some recent and related work on allyl complexes of main group metals is briefly mentioned.²

I

ALLYL COMPLEXES OF THE TRANSITION METALS

The complexes under this heading may be classified as σ -allyl (σ -C₃H₅) and π -allyl (π -C₃H₅) complexes, and allyl bridged complexes (μ -C₃H₅).

In the σ -allyl complexes the allyl radical, CH₂=CH—CH₂·, contributes one electron to the metal–allyl bond to give a conventional carbon–metal electron-pair linkage.

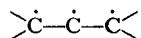
In the π -allyl compounds the allyl radical may be regarded as the contributor of three electrons to the metal–allyl bond. In general this results in a stronger bond between the metal and the allyl ligand than for the σ complexes.³

¹ Deceased.

² Earlier reviews which discuss allyl metal compounds may be found in refs. (3, 11, 13, 33a, 44, 82, 106).

³ It is, of course, equally possible to treat these complexes as involving donation of four electrons by an allyl anion. Thus, for example, in the complex (π -C₃H₅)₂Ni, nickel may be regarded as being either in oxidation state (II) or in oxidation state (0).

A theoretical treatment of the π -allyl bond is given in Section I,B,2. Those compounds, containing a conjugated three-carbon system



attached to the metal, are called π -allyl or π -allylic complexes.

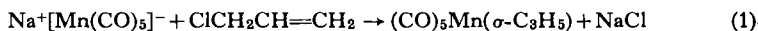
There is also some evidence that the allyl group may act as a bridge between two metals in certain complexes.

A. σ -Allyl Transition Metal Complexes

1. Preparation

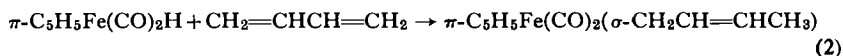
There are two main preparative routes to σ -allyl complexes, both of which involve standard methods for preparing metal-carbon σ bonds.

a. Reaction of Sodium Metal Carbonyls with Allyl Halides. Treatment of the sodium salt of a suitable metal carbonyl with an allyl halide gives the σ -allyl complex.



Better yields may be obtained in these reactions if the sodium salt is added to the allyl halide. Those π -allyl complexes which have also been prepared using this type of reaction (see below) almost certainly form via an unstable σ -allyl intermediate.

b. Addition of Metal Hydride Complexes to Conjugated Dienes. Substituted σ -allyl complexes may be prepared by addition of certain metal hydride complexes to conjugated dienes, e.g.,



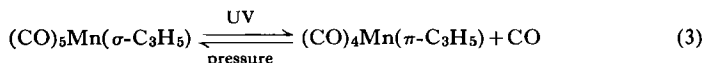
Known examples of this reaction involve 1:4 addition of the M—H bond across the diene, the product being a mixture of *cis* and *trans* isomers.

c. Formation from π -Allyl Complexes. In addition to the two previously mentioned methods of general applicability, studies of the nuclear magnetic resonance spectra of some π -allylpalladium complexes in dimethylsulfoxide (9) or dimethyl sulfide (96a) solution suggest that the π -allyl system is partially displaced from the metal and a σ -allyl complex is formed. The σ -allyl complexes have not been isolated from solution since removal of the solvent leads to the reformation of the π -allyl complex (9). Another example of this partial displacement reaction is given below in Eq. (3).

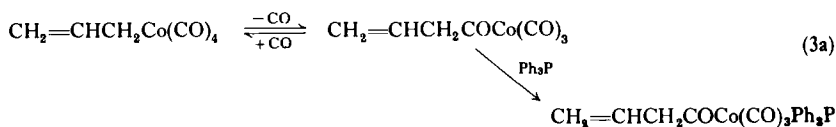
Since π -allyl complexes are considerably more abundant than σ -allyl complexes, it would seem reasonable that, using suitable ligands, a number of stable σ -allyl complexes may be preparable by this route.

2. Properties and Reactions of σ -Allyl Complexes

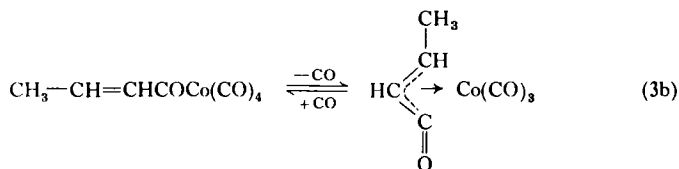
A list of known σ -allyl complexes of transition metals is given in Table I. All the known compounds are yellow oils which are insoluble in water, but very soluble in nonpolar solvents, such as petroleum ethers or benzene. Both the pure complexes and, especially, their solutions are oxidized by atmospheric oxygen, as are the closely related σ -alkyl metal complexes. The σ -allyl complexes are, in general, more unstable thermally than the analogous σ -alkyl metal complexes since they may decompose either by the same route involving breakage of the metal-carbon bond or by the formation of π -allyl complexes [see Eq. (3)]. Irradiation of any of the reported σ -allyl metal carbonyl complexes with ultraviolet light results in the displacement of carbon monoxide from the metal and formation of a π -allyl derivative, e.g.,



Carbonyl insertion reactions may also occur, and detailed studies of the reaction of the very unstable σ -allylcobalt tetracarbonyl with carbon monoxide and triphenylphosphine show the formation of butenoyl complexes via a 16-electron cobalt tricarbonyl intermediate (3a) (45, 50), *viz*:



It is interesting to note that in the case of some crotonylcobalt tetracarbonyl complexes the infrared spectra indicates that they are in equilibrium with π -crotonylcobalt tricarbonyl complexes (45).



The reaction (3b) may be compared with reaction (3).

TABLE I
 σ -ALLYL COMPLEXES OF TRANSITION METALS

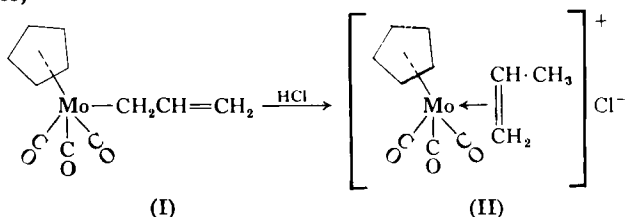
Formula	Properties	References concerning		
		Infrared	NMR	Preparation
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3(\sigma\text{-C}_3\text{H}_5)$	Yellow oil, m.p. -5°C , $d > 60^\circ$	14	14	14 ^a
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\sigma\text{-C}_3\text{H}_5)$		42	42	42 ^a
$\text{Mn}(\text{CO})_5(\sigma\text{-C}_3\text{H}_5)$	Yellow liquid, b.p. 45°C , 5 mm	79, 62	79, 62	79, 62 ^b
$\text{Mn}(\text{CO})_5(\sigma\text{-CH}_2\text{—CH=CH—CH}_3)$	Yellow liquid, b.p. 48°C , 2 mm	79	—	79 ^{a, b}
$\text{Mn}(\text{CO})_5(\sigma\text{-CH}_2\text{—CH=CH—Cl})$	Yellow liquid, b.p. 50°C , 0.5 mm	—	—	79 ^b
$\text{Mn}(\text{CO})_5(\sigma\text{-CH}_2\text{—CH}_2\text{=C(CH}_3)_2)$	Yellow liquid, b.p. $50\text{--}51^\circ\text{C}$, 2.0 mm m.p. $12\text{--}14^\circ\text{C}$	—	—	79 ^b
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\sigma\text{-C}_3\text{H}_5)$	Caramel liquid, $d > 60$	38	38	38 ^b
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\sigma\text{-CH}_2\text{—CH=CH—CH}_3)$	Caramel liquid, $d > 65$	38	38	38 ^a
$(\text{DMSO})_2\text{CIPd}(\sigma\text{-C}_3\text{H}_5)$ $(\text{DMSO})_2\text{CIPd}(\sigma\text{-CH}_2\text{—CH=CH—CH}_3)$ $(\text{DMSO})_2\text{CIPd}(\sigma\text{-CHCl—CH=CH}_2)$ $(\text{DMSO})_2\text{CIPd}(\sigma\text{-CH}_2\text{—CCl=CH}_2)$ $(\text{DMSO})_2\text{CIPd}(\sigma\text{-CH}_2\text{—CBr=CH}_2)$	Only present in a solution of dimethyl sulfoxide	9	9	9 ^c

^a Treatment of the Na(Li) salt with the allylic halide.

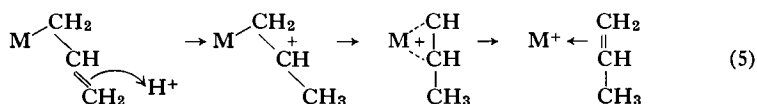
^b Treatment of the hydride with a diene.

^c From π -allyl complex by displacement with a strongly coordinating ligand.

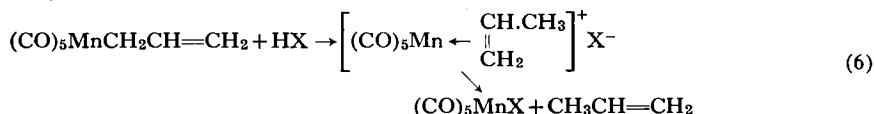
Another reaction which appears to be general for σ -allyl complexes is their facile protonation with acids, thereby affording novel π -ethylenic metal complexes,



It has been shown that the proton adds to the C-3 atom and the following mechanism has been proposed (38):



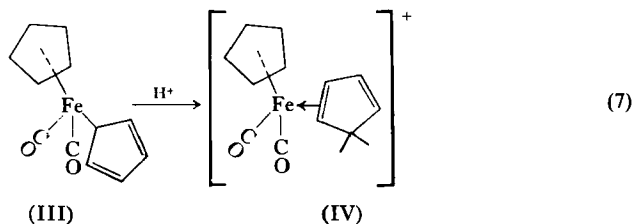
The facility with which the reaction proceeds may indicate that there is some interaction of metal electrons with the antibonding π orbitals of the ethylenic system of the σ -allyl group. In some cases the protonation reaction (5) may proceed further, resulting in displacement of the olefin by the anion of the salt,



With σ -allylmanganese pentacarbonyl the reaction stops at the first stage if $\text{X}^- = \text{ClO}_4^-$. However, when $\text{X}^- = \text{NO}_3^-$, Cl^- , CF_3COO^- , or HSO_4^- , a manganese pentacarbonyl salt is formed and propene is evolved (37).

3. σ -Cyclopentadienyl Complexes

σ -Cyclopentadienyl complexes may be regarded as rather special examples of σ -allyl systems. The complex $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$ has, for example,

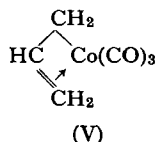


been shown to undergo a protonation reaction similar to that discussed above. The π -cyclopentadiene complex (IV) is formed in high yield (39).

σ -Cyclopentadienyl metal complexes have been reviewed elsewhere (13).

B. π -Allyl Transition Metal Complexes

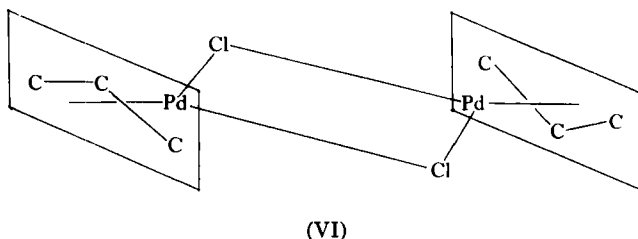
The field of both σ - and π -allyl complexes was brought into focus⁴ following studies by Jonassen and co-workers on the complex $C_4H_7Co(CO)_3$, which they prepared by treating hydrido-cobalt tetracarbonyl with butadiene. An early structural proposal for this complex was shown in (V) (59).



After the difficulties of separating the two isomers formed in the reaction were overcome, proton magnetic resonance studies provided the necessary evidence for the now accepted "sandwich" structure of the π -allylmethyl system (1, 81). Essentially concurrent with these studies, other workers prepared allyl complexes of cobalt and manganese (52, 51, 77, 63), and, again primarily using the evidence of proton magnetic resonance spectra, they similarly proposed the "sandwich" structure.

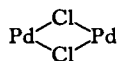
1. Structure of π -Allyl Metal Complexes

a. *X-Ray Studies.* X-ray studies (95) on the complex $(\pi-C_3H_5PdCl)_2$ (VI) establish the structure shown.



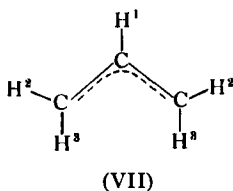
⁴ The expression "brought into focus" is used since, prior to these studies, a number of organometallic complexes were described in the literature, particularly those of palladium, which were incorrectly formulated, often as olefin complexes. Only recently have these compounds been recognized as π -allylic complexes.

In this complex, the carbon-carbon bonds are *equal* in length, both being 1.3 ± 0.1 Å. The three carbons lie in a plane which is perpendicular to the plane through the



system. The palladium-carbon distances are all 2.1 ± 0.05 Å, and the terminal carbon atoms are about 0.1 Å below the $(\text{PdCl})_2$ plane while the central carbon is about 0.4 Å above the plane.

b. Proton Magnetic Resonance Studies. The spectra of a large number of π -allyl complexes have been measured. They are all essentially similar and may best be interpreted in terms of the "sandwich" structure (82). The customary numbering of the protons of the π -allyl group is shown in (VII),

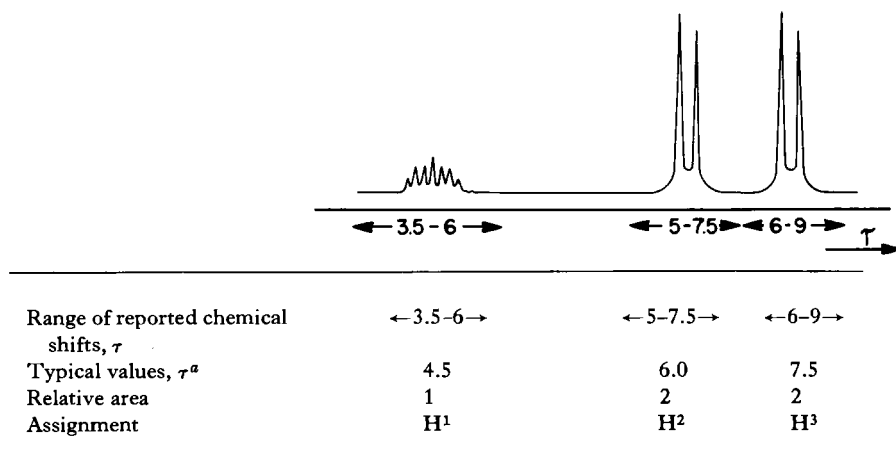


and a model spectrum and some general data are presented in Fig. 1 and Table II. Fortunately, in all the reported spectra chemical shifts between the non-equivalent protons are considerably greater than the values of the various coupling constants, and therefore a first-order interpretation of the spectra is legitimate. Moreover, for a few compounds, calculations have justified this assumption and shown that the spectra may be interpreted on the basis of an AM_2X_2 system (16). Observed values of \mathcal{J}_{12} and \mathcal{J}_{13} correspond to typical values of *cis*- and *trans*-coupling constants, respectively, in substituted ethylenes (2). The value of \mathcal{J}_{23} is nearly always small—as is also found in substituted ethylenes, only in the case of π -2-chloroallylpalladium complexes has coupling between the H^2 and H^3 hydrogens been observed ($\mathcal{J}_{23} = 2$ cps) (74b). Karplus and Anderson have shown (64, 65) that the nonperfect pairing valence bond structures make the major contribution to the contact coupling constants. Thus, the absence of coupling between H^2 and H^3 suggests that either interference by the metal orbitals has reduced the contribution of the nonperfect pairing structures to the ground state wave function, or the HCH dihedral angle is near to 125° , in which case the value of \mathcal{J}_{23} is zero (43, 82).

If the hydrogen atoms of the π -allyl group lie in the plane of the carbon atoms, as seems reasonable, then the occurrence of the H^3 hydrogens at higher fields than the H^2 hydrogens may be due to differential shielding of the hydrogens by the metal atom. It may be noted that the π -allyl complex $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3(\pi\text{-C}_3\text{H}_5)$ and the tungsten analog (14, 42) are exceptional in that there is a marked broadening of the doublet assigned to the H^3

FIG. 1. AND TABLE II

Appearance of a typical proton magnetic resonance spectrum of a π -allyl metal group with range τ values.



^a $J_{12} \sim 7$ cps; $J_{13} \sim 11$ cps; $J_{23} \sim 0$ cps.

hydrogens. It has been suggested that this may be due to a nonequivalent interaction of the H^3 hydrogens with the metal or other ligands in the molecule.

The spectrum of a π -allyl system where H^1 has been substituted is often very simple but when substitution at H^2 or H^3 occurs considerably more complex spectra are observed. Nonetheless, the spectrum of π -crotyl-palladium chloride can be interpreted satisfactorily on the basis of an AMM'X system (16, 44). In some cyclohexenyl complexes of palladium, the H^3 hydrogens are substituted by a $(\text{—CH}_2\text{—})_3$ group. A comparison of their spectra with those of analogous π -allyl complexes confirms the assignments of the H^3 hydrogens to the higher doublet in the spectra of the unsubstituted complexes (33, 61, 99). In the case of the platinum complex

$\pi\text{-C}_3\text{H}_5\text{Pt}(\pi\text{-C}_5\text{H}_5)$, secondary splittings arise due to coupling with the Pt^{195} nucleus (99). Recently, the spectra of some π -allylpalladium complexes, where H^1 is substituted by a methyl group and an H^2 by the group $-\text{C}(\text{CH}_3)_2\text{OCH}_3$, have shown that there is restricted rotation about the carbon— $\text{C}(\text{CH}_3)_2\text{OCH}_3$ bond (94a). Proton magnetic resonance spectra, therefore, can provide strong evidence for the presence in a metal complex of a π -allylic system. However, since anomalous spectra are occasionally found for organometallic complexes, such data should always be evaluated with care.

c. Infrared Spectra. The spectra of π -allyl complexes are in general consistent with the proposed configuration. References to reported spectra are given in Table IV. Fritz (34) has studied the spectra of a number of allylic complexes of palladium and nickel and, assuming the sandwich configuration, has made a number of assignments for the allylic system. For the π -allylpalladium complex (VI) a medium intensity band at 1458 cm^{-1} is assigned to the delocalized C—C stretch (ω_{CC}) and weak bands above 1500 cm^{-1} are assigned to combination overtones. The $\text{CH}_2(\parallel)$ and $\text{CH}(\parallel)$ (in-plane) deformations occur between 1200 and 1450 cm^{-1} and the $\text{CH}(\perp)$ and $\text{CH}(\perp)$ (out-of-plane) deformations are found below 1000 cm^{-1} . It has been suggested that the skeletal deformations (Δ_{CCC}) which occur at 511 cm^{-1} in the complex (VI) may be used to recognize the presence of a π -allylic system. However, since only a few spectra of these complexes have been recorded below 700 cm^{-1} , it remains uncertain whether this band has any real diagnostic value.

There is some disagreement concerning assignment of the C—H stretches (16, 34). Fritz suggests that there is some interaction of the H^3 hydrogen atoms with the metal. This could cause a lowering of the C—H stretch, in a manner similar to the lowering of the C—H *endo* stretches of some μ -bonded cyclopentadiene-metal complexes (41, 61).

2. Theoretical Treatment of the Bonding in π -Allyl Metal Systems

Evidence for the structure of π -allylpalladium dichloride (VI) shows that the terminal carbons are equivalent and that the three carbons are in a plane facing the metal. The simplest description of the bonding between the π -allyl group and the palladium atom is one which is somewhat analogous to the description given for the π -ethylene-platinum system (8). In complex (VI) the π -allyl group has the symmetry C_{2v} and the carbon $2p$ orbitals transform under C_{2v} symmetry as $A_1 + 2B_1$ irreducible representations.

Also, a straightforward Hückel calculation (101) shows that the $2p_z$ orbitals of the allyl carbon atoms can form three molecular orbitals, which are

$$\psi_1 = \frac{1}{2}\phi_1 + \sqrt{\frac{1}{2}}\phi_2 + \frac{1}{2}\phi_3$$

$$\psi_2 = \sqrt{\frac{1}{2}}\phi_1 - \sqrt{\frac{1}{2}}\phi_3$$

$$\psi_3 = \frac{1}{2}\phi_1 - \sqrt{\frac{1}{2}}\phi_2 + \frac{1}{2}\phi_3$$

where the symbols have their usual meaning (101). These molecular orbitals may be represented as in Fig. 2.

In order to determine which of the metal orbitals may interact with the molecular orbitals of the allyl ligand it is necessary to make several assumptions. Brown (7) and Orgel (88) used the approximation that it is permissible to classify the metal electrons under the local symmetry of the attached ligand. Hence, since only orbitals of the same symmetry may combine, the possible bonding and nonbonding orbitals may be separated. These are shown in Table III.

TABLE III
ORBITALS FOR π -ALLYL SYSTEMS

π -C ₅ H ₅ -Pd	Bond type	Nonbonding	PdCl
$(\psi_1 + s + d_{z^2} - p_z)^2$	σ	$(s - d_{z^2})^2$	$(Cl_{2a} + s + d_{z^2} + p_z)^2$
$(\psi_2 + d_{xz} - p_x)^2$	π	—	$(Cl_{2b} + d_{xz} + p_x)^2$
$(\psi_3 + d_{yz} - p_y)^2$	π	$(d_{xy})^2 (d_{x^2-y^2})^2$	—

The extent to which the π -allyl metal orbitals shown above will form strong bonds depends on the relative energies of the ligand and metal orbitals. A rough estimate of these energies, based on the ionization potentials of the allyl radical and of palladium metal, suggest that the strongest bond is likely to arise from the interaction between the ψ_1 and the ψ_2 orbitals with the metal orbitals. In other words, the allyl group may be considered to bond to the metal by a σ bond and π bond in a pictorially somewhat similar way to that proposed for the π -ethylene-platinum system.

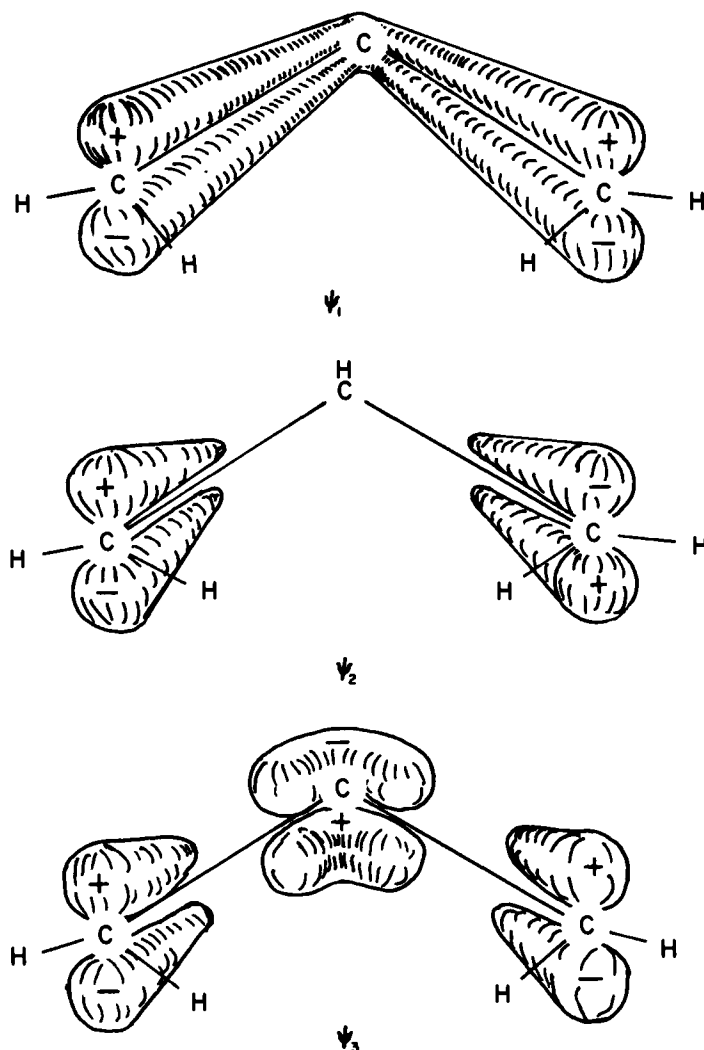


FIG. 2. Pictorial representation of the molecular orbitals ψ_1 , ψ_2 , and ψ_3 of the allyl systems.

3. The Occurrence of π -Allyl and Related Complexes

All complexes in this class reported prior to January 1st, 1964, are given in Table IV. It is convenient when discussing the preparation and properties of π -allylic complexes to separate them into two categories. The

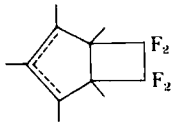
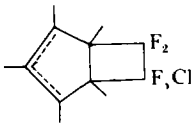
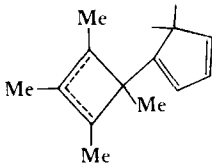
TABLE IV.

π -Bonded allylic group	Formula	Color and form ^a
Tris(allyl)	$(\pi\text{-C}_3\text{H}_5)_3\text{Cr}^b$	Deep red x
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Cr}-\pi\text{-C}_5\text{H}_5(\text{CO})_2$	Orange x
Cyclopentenyl	$\pi\text{-C}_5\text{H}_7\text{Cr}-\pi\text{-C}_5\text{H}_5(\text{CO})_2$	Yellow x
Allyl	$\pi\text{-C}_3\text{H}_5\text{Mo}-\pi\text{-C}_5\text{H}_5(\text{CO})_2$	Yellow x
Allyl	$\pi\text{-C}_3\text{H}_5\text{W}-\pi\text{-C}_5\text{H}_5(\text{CO})_2$	Yellow x
Allyl	$\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_4$	Pale yellow x
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Mn}(\text{CO})_4$	Yellow liq.
2-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Mn}(\text{CO})_4$	Yellow liq.
1,1-Dimethylallyl	$\pi\text{-C}_5\text{H}_9\text{Mn}(\text{CO})_4$	Yellow liq.
1-Chloroallyl	$\pi\text{-C}_3\text{H}_4\text{ClMn}(\text{CO})_4$	Yellow liq.
Tris(allyl)	$(\pi\text{-C}_3\text{H}_5)_3\text{Fe}^b$	Golden brown x
Allyl	$\pi\text{-C}_3\text{H}_5\text{FeC}_5\text{H}_5(\text{CO})$	Yellow x
Allyl	$\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}^{b, e}$	Yellow-brown x
Allyl	$\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Br}^{b, e}$	Yellow-brown x
Allyl	$\text{C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}^{b, e}$	Dark brown x
1-Bromoallyl	$\pi\text{-C}_3\text{H}_4\text{BrFe}(\text{CO})_3\text{Br}$	Red-brown x
2-Bromoallyl	$\pi\text{-C}_3\text{H}_4\text{BrFe}(\text{CO})_3\text{Br}$	Yellow-brown x
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Fe}-\pi\text{-C}_5\text{H}_5\text{CO}^f$	Caramel liq.
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Fe}(\text{CO})_3\text{Cl}^g$	Yellow x
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Fe}(\text{CO})_3\text{Br}$	Yellow-brown x
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Fe}(\text{CO})_3\text{I}$	Red-brown x
1-Methylallyl	$[\pi\text{-C}_4\text{H}_7\text{Fe}(\text{CO})_3]^+\text{BF}_4^{-g, h}$	Yellow x
2-Methylallyl	$[\pi\text{-C}_4\text{H}_7\text{Fe}(\text{CO})_4]^+\text{Cl}^-$	Yellow powder
2-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Fe}(\text{CO})_3\text{I}$	Dark brown
1,1-Dimethylallyl	$[\pi\text{-C}_5\text{H}_9\text{Fe}(\text{CO})_3]^+\text{BF}_4^{-g, h}$	Yellow x
1,3-Dimethylallyl	$[\pi\text{-C}_5\text{H}_9\text{Fe}(\text{CO})_3]^+\text{BF}_4^{-g, h}$	Yellow x
1-Acetatoallyl	$\pi\text{-C}_5\text{H}_7\text{O}_2\text{Fe}(\text{CO})_3\text{Br}$	Yellow-brown x
Tris(allyl)	$(\pi\text{-C}_3\text{H}_5)_3\text{Co}^b$	Golden-red x
Allyl	$\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$	Orange liq.
Allyl	$[\pi\text{-C}_3\text{H}_5\text{Co}-\pi\text{-C}_5\text{H}_5(\text{CO})]^+\text{PF}_6^{-h}$	Yellow powder
Allyl	$\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$	Yellow x
Allyl	$\pi\text{-C}_3\text{H}_5\text{CoC}_5\text{H}_5\text{I}$	Dark red x
Allyl	$\pi\text{-C}_3\text{H}_5\text{CoC}_5\text{H}_5\text{Br}$	Red x
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Co}(\text{CO})_3^f$	Orange liq.
1-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$	Orange x
2-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Co}(\text{CO})_3$	—
2-Phenylallyl	$\pi\text{-C}_9\text{H}_9\text{Co}(\text{CO})_3$	—
1-Carbomethoxyallyl	$\pi\text{-C}_5\text{H}_7\text{O}_2\text{Co}(\text{CO})_3$	—

π -ALLYL COMPLEXES

M.p. or (b.p./mm) (°C)	References concerning			Comments
	Preparation	Infrared spectra	NMR spectra	
—	(103)	—	—	
118–121	(25 ^b)	—	—	
74–75	(27 ^a , 28 ^c)	(27, 28)	(27)	3.49D C ₆ H ₆ (27)
134 (dec)	(14)	(14)	(14)	
—	(42)	(42)	(42)	
55–56 (97)	(62, 79)	(62, 79)	(62, 79)	
52–53.5 (62)				
(68/7)	(79)	(79)	(79)	
(50/2.5)	(79)	(79)	(79)	
(48–52/1)	(79)	(77)	(77)	
(85/6)	(79)	(79)	(79)	
—	(104)	—	—	
65 (dec)	(38)	(38)	(38)	
88–89	(83)	(83)	—	
86–87	(83)	(83)	—	
85–86	(83, 93)	(83, 93)	(93)	
79–80	(83)	(83)	—	
84–85	(83)	(83)	—	
> 60 (dec)	(38)	(38)	(38)	
58–60	(56, 83, 102)	(56, 83)	(56)	
34.5	(83)	(83)	—	
50–53	(83)	(83)	—	
—	(19)	(19)	—	16 electron
—	(48)	(48)	(48)	
100	(93)	(92, 93)	(93)	
—	(19)	—	(19)	16 Electron
—	(19)	—	(19)	16 Electron
65	(83)	(83)	—	
—	(103)	—	—	
M.p. — 33 (39.15 mm)	(50, 51, 52, 77)	(51, 52, 77)	(51, 52, 77)	Kinetics of CO displacement (45)
110 (dec)	(24)	(24)	—	
132 (dec)	(50, 51, 52)	(51)	—	
95.5–97	(48)	(48)	(48)	
96–98	(48)	—	(48)	
(36/4–5)	(1, 59)	(1)	(77, 81)	
91.5–94	(51)	(51)	—	
—	(45, 47)	(45, 47)	—	
—	(45, 47)	(45)	—	
—	(45, 47)	(45, 47)	—	

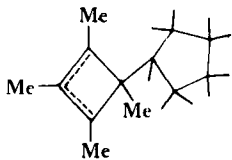
TABLE IV

π -Bonded allylic group	Formula	Color and form ^a
1-Chloroallyl	$\pi\text{-C}_3\text{H}_4\text{ClCo(CO)}_3$	Amber liq.
2-Chloroallyl	$\pi\text{-C}_3\text{H}_4\text{ClCo(CO)}_3$	Amber liq.
2-Bromoallyl	$\pi\text{-C}_3\text{H}_4\text{BrCo(CO)}_3$	—
Bis(allyl)	$(\pi\text{-C}_3\text{H}_5)_2\text{Ni}$	Orange-yellow x
Bis(1-methylallyl)	$(\pi\text{-C}_4\text{H}_7)_2\text{Ni}$	Brown-yellow x
Bis(2-methylallyl)	$(\pi\text{-C}_4\text{H}_7)_2\text{Ni}$	Brown-yellow x
Allyl	$\pi\text{-C}_3\text{H}_5\text{NiCl(CO)}^b$	Orange solid
Allyl	$[\pi\text{-C}_3\text{H}_5\text{NiBr}]_2$	Red x
Allyl	$[\pi\text{-C}_3\text{H}_5\text{NiI}]_2$	Dark red x
Allyl	$\pi\text{-C}_3\text{H}_5\text{Ni-}\pi\text{-C}_5\text{H}_5$	Red liq.
Allyl	$\pi\text{-C}_3\text{H}_5\text{Ni(Cl)P(C}_6\text{H}_5)_3$	Red x
2-Methylallyl	$\pi\text{-C}_4\text{H}_7\text{Ni(Cl)P(C}_6\text{H}_5)_3$	Red x
Cyclopentenyl	$\pi\text{-C}_5\text{H}_7\text{Ni-}\pi\text{-C}_5\text{H}_5$	Red x
Methylcyclopentenyl	$\pi\text{-C}_5\text{H}_7\text{Ni-}\pi\text{-C}_5\text{H}_5$	Red liq.
	$\pi\text{-C}_7\text{H}_5\text{F}_4\text{Ni-}\pi\text{-C}_6\text{H}_5^g$	Red x
	$\pi\text{-C}_7\text{H}_5\text{F}_3\text{ClNi-}\pi\text{-C}_6\text{H}_5^f$	Red x
	$\pi\text{-C}_{13}\text{H}_{17}\text{Ni-}\pi\text{-C}_6\text{H}_5$	Red x

—continued

M.p. or (b.p./mm) (°C)	References concerning			Comments
	Preparation	Infrared spectra	NMR spectra	
(38/2)	(77)	(77)	(77)	
(30/2)	(45, 47)	(45, 47)	—	
—	(45, 47)	—	—	
—	(103, 104)	(104)	(104)	Mass spectrum(104)
—	(103)	—	—	
—	(103)	—	—	
—	(10, 49)	—	—	
93–95 (dec)	(20)	(20)	—	$1.31 \pm 0.06D$ C ₆ H ₆ (20)
118–120 (dec)	(22)	(22)	—	$1.62 \pm 0.07D$ C ₆ H ₆ (22)
(40/0.05)	(20, 22)	(79)	(79)	
140–150 (dec)	(49)	(49)	—	
—	(49)	(49)	—	
42–43	(17, ^a 32 ^c)	(32, 34)	(17, 30, 33, ^c 61, ^c 99 ^d)	$1.16 \pm 0.07D$ C ₆ H ₁₂ (32)
38–39 (vac)	(30)	(30)	(30)	$1.20 \pm 0.05D$ C ₆ H ₆ (30)
93–94	(77)	—	(77 ^e)	
68–73	(77)	—	(77 ^e)	
75	(15, ^c 68 ^f)	(15, 68)	(68)	X-ray structure (68)

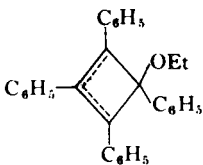
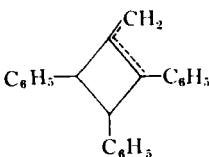
TABLE IV

π -Bonded allylic group	Formula	Color and form ^a
	$\pi\text{-C}_{13}\text{H}_{21}\text{Ni-}\pi\text{-C}_5\text{H}_5^b$	Red x
Dodeca-1,11-dienyl-6-ene	$\pi\text{-C}_{12}\text{H}_{18}\text{Ni}$	Red brown x
Bis(allyl)	$(\pi\text{-C}_3\text{H}_5)_2\text{Pd}^b$	Straw yellow x
Allyl	$\pi\text{-C}_3\text{H}_5\text{Pd-}\pi\text{-C}_5\text{H}_5$ [substituted derivatives (94a)]	Dark red x
Allyl	$\pi\text{-C}_3\text{H}_5\text{Pd-}\pi\text{-C}_5\text{H}_4\text{R}$ R = Me, Et, Pr ⁿ	Red
Allyl	$(\pi\text{-C}_3\text{H}_5\text{PdX})_2$ where X = Cl, Br, and I	Yellow-deep yellow x
Allyl	$\pi\text{-C}_3\text{H}_5\text{Pd(Cl)L}$ where L = Br, I, SCN, <i>p</i> -tol	Yellow x
1-Chloroallyl	$[\pi\text{-C}_3\text{H}_4\text{ClPdCl}]_2$	Yellow x
2-Chloroallyl	$[\pi\text{-C}_3\text{H}_4\text{ClPdCl}]_2$	Yellow x
2-Bromoallyl	$[\pi\text{-C}_3\text{H}_4\text{BrPdCl}]_2$	—
1-Methylallyl	$[\pi\text{-C}_4\text{H}_7\text{PdCl}]_2$	Yellow x
2-Methylallyl	$[\pi\text{-C}_4\text{H}_7\text{PdCl}]_2$	Yellow x
1-Chloromethylallyl	$[\pi\text{-C}_4\text{H}_6\text{ClPdCl}]_2$	Yellow
1-Methoxy-1-methylallyl	$[\pi\text{-C}_4\text{H}_6\text{OCH}_3\text{PdCl}]_2$	Yellow x
Cyclohexenyl	$\pi\text{-C}_6\text{H}_9\text{Pd-}\pi\text{-C}_5\text{H}_5$	Red x
Cyclohexenyl	$\pi\text{-C}_6\text{H}_9\text{Pd-}\pi\text{-CH}_3\text{C}_5\text{H}_4$ $[\pi\text{-C}_6\text{H}_9\text{PdCl}]_2$	Red x Yellow x
1-Methoxyl-2-methylallyl	$[\pi\text{-C}_6\text{H}_9\text{OPdCl}]_2^m$	Yellow x
1-Methoxyl-2-methylallyl	$\pi\text{-C}_6\text{H}_9\text{OPd(Cl)P(C}_6\text{H}_5)_3^f$ also where ligand = NC ₆ H ₇	Yellow x
1-Methylcyclohexenyl	$(\pi\text{-C}_7\text{H}_{11}\text{PdCl})_2$	Yellow x
Diisobutenyl	$(\pi\text{-C}_8\text{H}_9\text{PdCl})_2$	Yellow x
α -Methylstyryl	$(\pi\text{-C}_8\text{H}_9\text{PdCl})_2$	Yellow x
β -Methylstyryl	$(\pi\text{-C}_9\text{H}_9\text{PdCl})_2$	Yellow x
1-Methyl-1-methyl-methoxylallyl	$[\pi\text{-C}_9\text{H}_{17}\text{O)Pd-}\pi\text{-C}_5\text{H}_5$	Red x

—continued

M.p. or (b.p./mm) (°C)	References concerning			Comments
	Preparation	Infrared spectra	NMR spectra	
51	(15)	—	—	
—	(10)	—	—	
—	(103)	—	—	
64	(28, 71, 94, 99)	(34)	(77, 99)	
—	(94, 94a)	—	—	
145–200	(21, 54, 55, 79, 80, ^k 100)	(21, 34)	(9, 16, 64, 79, 80, 99)	X-ray (95) 2.18D C ₆ H ₆ when X = Br (21)
—	(44)	—	—	
179 (dec)	(9)	—	(9)	
175 (dec)	(9)	—	(9)	
—	(9, 96a, 74b) ^l	—	(9)	
164	(100, 96a)	(16, 34)	(16)	
—	(55, 100)	(34)	(99)	
120 (dec)	(97, 94a)	—	(97)	
97–98	(97, 94a)	—	(97)	
69 (80, dec)	(30, 31 ^c)	(31, 34)	(30, 33 ^a , 60, 99 ^d)	2.05 ± 0.04D C ₆ H ₆ (31)
1–3, d > 20	(30 ^c)	(30, 34 ^d)	(60, ^a 99)	
85–95	(30, ^a 31, ^c 55 ^d)	(34 ^d)	(60 ^d)	
210 (dec)	(79, 80, 89)	(90)	(90)	
175 (dec)	(90)	(90)	(90)	
69	(55)	—	—	
204	(55)	—	—	
220–230	(55)	—	—	
195–200	(55)	—	—	
57–58	(97)	—	—	

TABLE IV

π -Bonded allylic group	Formula	Color and form ^a
α -Dimethylstyryl	$[\pi-(C_{10}H_{11}PdCl)]_2$	Yellow x
Methylstilbenyl	$[\pi-(C_{15}H_{13})Pd]_2$	Yellow
Triisobutenyl	$(\pi-C_{12}H_{15}PdCl)_2$	Yellow x
	$[\pi-C_{30}H_{25}OPdCl]_2^b$	—
	$[(\pi-C_4R_3CH_2)PdCl]_2^b$	—
Allyl	$\pi-C_3H_5Pt-\pi-C_5H_5$	Lemon yellow

^a x indicates a crystalline solid.^b Not fully characterized.^c Incorrect structure formulated.^d Structure correctly reformulated.^e There are indications of a monomer-dimer equilibrium in solution, where the dimers may have bridging allyl groups.^f Present as a mixture of isomers.

—continued

M.p. or (b.p./mm) (°C)	References concerning			Comments
	Preparation	Infrared spectra	NMR spectra	
170–175	(55)	—	—	
230–235	(55)	—	—	
125	(55)	—	—	
—	(45, 75)	(45, 75, 76)	—	
—	(45, 75, 76)	—	—	
63–64	(98)	—	(98)	

^a Apparently only a single isomer present.

^b Salts of other anions also prepared.

^c F^{19} resonance spectrum also determined.

^d The X-ray structure by L. F. Dahl and co-workers is noted in this reference.

^e Isomers are described where X = Cl as yellow (α) and dark green (β) forms.

^f Many complexes where the 2—hydrogen is substituted by Cl or $-\text{C}(\text{CH}_2\text{Cl})=\text{CH}_2$ are given in references (74b, 96a). Examples are $\text{Pd}_2\text{I}_2(\text{C}_6\text{H}_8\text{Cl})_2$, Pd (ac ac) $\text{C}_6\text{H}_8\text{Cl}$ (74b).

^m Some incompletely characterized derivatives are also reported.

first category contains the π -allyl, π -methylallyl, and other similarly simply substituted π -allylic systems. These complexes may be discussed more or less systematically. The second category consists of a number of miscellaneous π -allylic-type complexes which are prepared by unique routes.

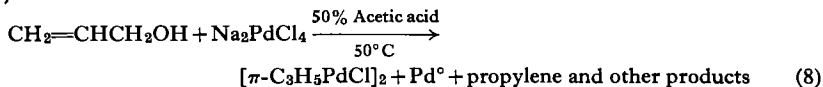
The various π -allylic-type ligands which have so far been recognized are shown in the first column of Table IV. At present more π -allylic complexes of palladium are known than of the other metals, but the preparation of π -allylic complexes of other metals is more a matter of time than chemistry in that similar complexes of most of the transition metals should be obtainable.

4. The Preparation of π -Allyl Transition Metal Complexes

There are several general methods available for preparing π -allyl or the more simply substituted π -allylic complexes. Of course, experimental precautions general to preparative organometallic chemistry, such as the exclusion of air from the reaction mixture, are normally essential in this work.

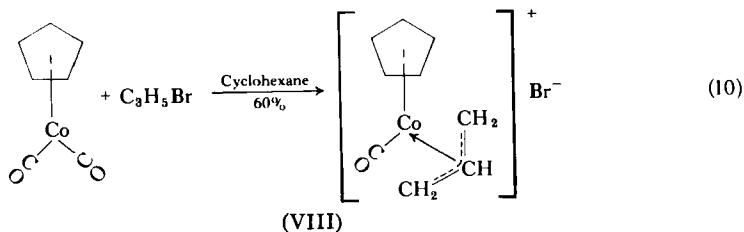
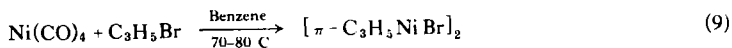
a. Reaction of Salts of Transition Metal Carbonyls with Allyl Halides. Treatment of suitable alkali metal salts of transition metal carbonyl complexes with an allyl halide, as discussed previously for the preparation of σ -allyl complexes (Section I, A,1,a), has also been used to obtain many π complexes. As mentioned, it may be necessary to decompose the intermediate σ -allyl complex by irradiation with ultraviolet light in order to obtain the desired π -allyl derivative. However, in many cases, for example, in the preparation of π -allylcobalt complexes, the σ -allyl complex is very unstable and decomposes at low temperatures and so only the π -allyl complex is isolated.

b. Reaction of Allyl Halide or Alcohol with Metal Halide or Carbonyl. Another common preparative method involves the direct reaction between an allyl halide or alcohol and a metal halide or metal carbonyl, (55, 80, 100), e.g.,



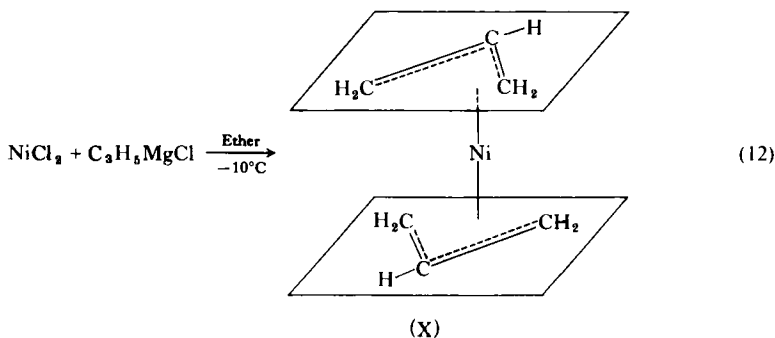
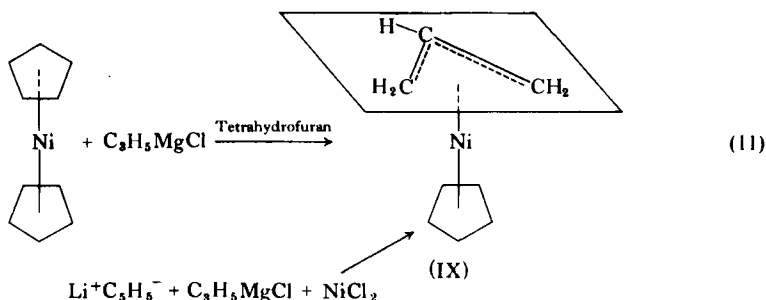
It has been shown that for palladium, the pure metal alone will react with allyl bromide to give the analogous bromide $[\pi\text{-C}_3\text{H}_5\text{PdBr}]_2$ in 40% yields (21).

Other examples of this reaction are



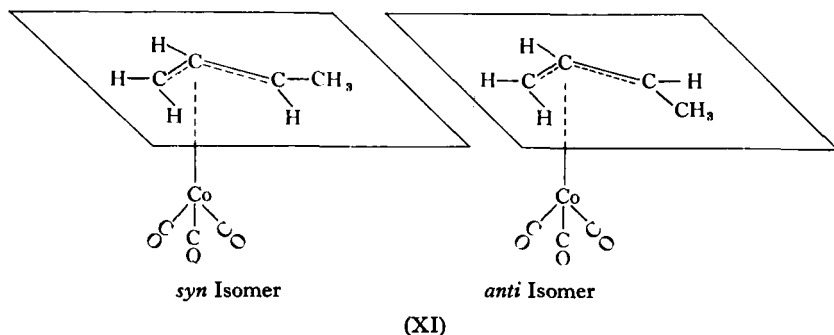
With π -cyclopentadienylcobalt dicarbonyl, it has been shown that when allyl iodide is used a neutral complex $\pi\text{-C}_5\text{H}_5\text{Co}(\pi\text{-C}_3\text{H}_5)\text{I}$ is formed in 10% yield, as well as the analogous iodide salt of complex (IV) (48). The reaction of chromocene with allyl iodide does not give an allyl complex (26).

c. Reaction of Allyl Grignard Reagents, with Metal Salts. The reaction of allyl Grignard reagents with metal salts has also been used (103, 104)



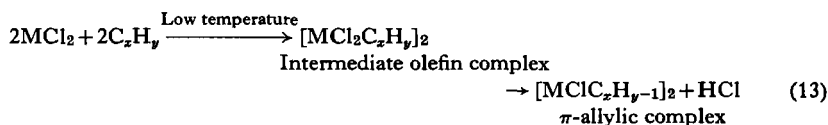
d. Addition of Transition Metal Hydrides to Dienes. Treatment of conjugated dienes with a transition metal hydride, as discussed for the σ -allyl complexes, can yield substituted π -allyl complexes. The complex $\text{C}_4\text{H}_7\text{Co(CO)}_3$

(discussed above, (Section I,B) is formed as a mixture of geometrical isomers of π -crotylcobalt tricarbonyl (XI) in this way.

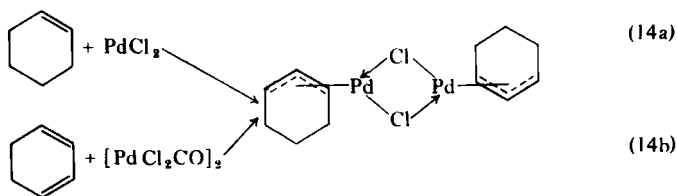


The *syn* isomer is thermally the more stable, and the *anti* isomer may be converted into the *syn* by equilibration at 80° C. The isomers may be distinguished by their proton magnetic resonance spectra (81).

e. Reaction of Olefins or Allenes with Metal Salts. (i) The reaction of an olefin with some metal salts can result in formation of a π -allyl metal complex. This reaction probably proceeds *via* prior formation of intermediate olefin-metal complexes. The process has been represented formally as shown in Eq. (13) (14).



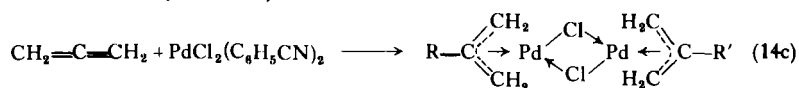
An example of this reaction is (14a)



In passing it is worth noting that in reaction (14b), which affords the same product, hydrogen has been acquired by the diene. The appearance, disappearance, and migration of hydrogen atoms in hydrocarbon ligands is a frequent but irregular phenomenon of preparative organometallic chemistry. As yet little is understood about the detailed mechanisms of these reactions

but it is known that, for example, transition metals will readily form covalent metal-hydrogen bonds and that organic groups attached to transition metals will often lose hydrogen, even as a hydride ion (36, 40). Since analysis cannot accurately determine the number of hydrogen atoms, because of the high molecular weight of the complexes, and since the proton magnetic resonance spectra of organometallic complexes are often too complex for an unequivocal assignment, the unsuspected gain or loss of a hydrogen atom often results in an initially incorrect formulation of particular complexes. Hence for an accurate description of the ligand attached to a transition metal it is often necessary to study in considerable detail the chemistry and spectral properties of the molecule, and sometimes, if possible, the spectra of substituted derivatives.

(ii) Treatment of some palladous salts with allenes affords π -allylic complexes. The investigations are at an early stage, however, it appears that the nature of the π -allylic complexes formed depends markedly on the reaction conditions (74b, 96a).

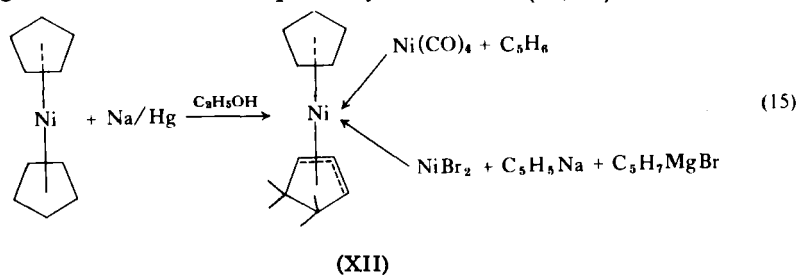


where (1) Allene not in excess; benzene solution; $\text{R} = \text{R}' = \text{Cl}$ (80%). (2) Allene in excess; benzene solution; $\text{R} = \text{Cl}$ and $\text{R}' = -\text{C}(\text{CH}_2\text{Cl})=\text{CH}_2$ (96.4%). (3) Allene in excess; benzonitrile solution; $\text{R} = \text{R}' = -\text{C}(\text{CH}_2\text{Cl})=\text{CH}_2$ (78.5%).

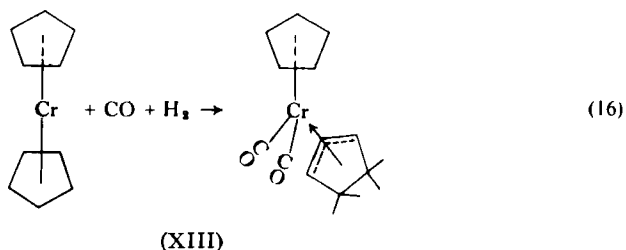
5. Some Specific Preparations of π -Allylic Complexes

Examples of some unusual π -allylic complexes which have been prepared by unique routes are given here.

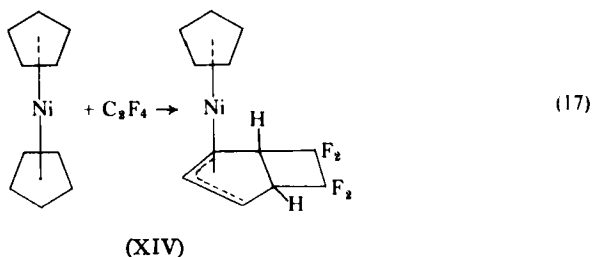
a. Reactions with Nickelocene. Reduction of nickelocene with sodium amalgam affords a π -cyclopentenyl ring. Thus, during the reduction, two hydrogen atoms have been acquired by nickelocene (17, 32).



Similarly, reduction of chromocene with hydrogen in the presence of carbon monoxide also affords a π -cyclopentenyl complex (27, 28).

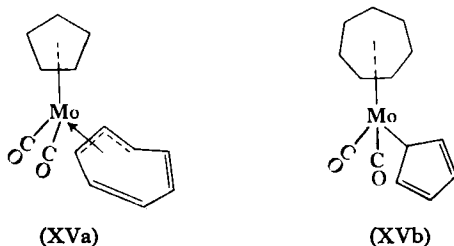


The reaction between tetrafluoroethylene and nickelocene affords a novel bicyclo- π -allylic complex (77).



The nuclear magnetic resonance spectrum shows that there is probably only one of the two possible isomers present, but the evidence at the moment cannot show whether the tertiary hydrogens are *exo* or *endo*, although other considerations favor *endo* hydrogens.

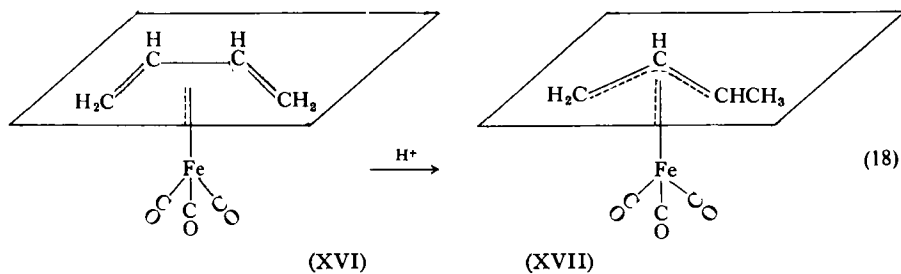
b. Reaction of Cycloheptatriene-Molybdenum Dicarbonyl Iodide (4) with Sodium Cyclopentadienide. This reaction affords an orange crystalline compound for which two structures (XVa and b) are possible (70).



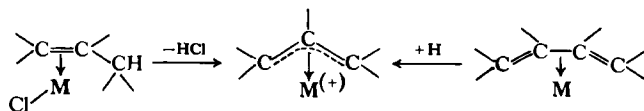
Proton magnetic resonance data cannot distinguish between the two structures since only two single resonance peaks are observed. It is to be noted

that σ -bonded cyclopentadienyl groups in certain metal complexes have been shown, surprisingly, to give only a single resonance band (92). Moreover, the compound cyclooctatetraene-iron tricarbonyl in solution shows a single resonance peak, even though in the crystalline state X-ray studies have established a structure in which protons are in several different environments. In view of these results it is possible that a π -allyl-bonded cycloheptatrienyl group might also give rise to a single resonance signal. However, arguments presented elsewhere (70) are slightly in favor of structure (XVa).

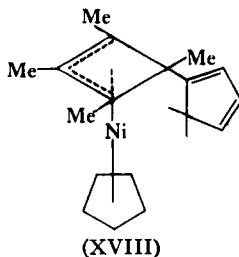
c. Protonation of Diene-Metal Complexes. Some diene-metal complexes have been shown to protonate readily, thereby forming π -allylic cations (19, 102). The reaction is somewhat analogous to the protonation of σ -allyl metal complexes (Eq. 5).



It is thus to be noted that π -allylic systems may be prepared either by the loss of a proton from a monoolefin complex (Section I,B,4,e) or by the addition of a proton to a diolefin complex, i.e.,



d. Treatment of Tetramethylcyclobutadienyl-nickel Dichloride with Sodium Cyclopentadienide. This reaction affords a volatile red solid (15) for which

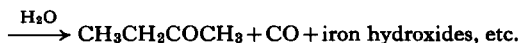
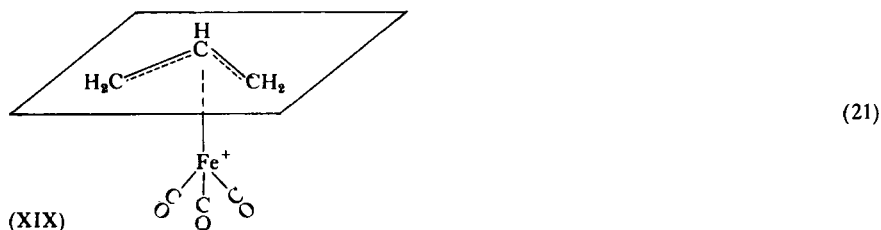


structure (XVIII) has been established, on the basis of X-ray crystallographic results (68). Earlier structures based on chemical studies (15) and proton magnetic resonance data (68) were incorrect.

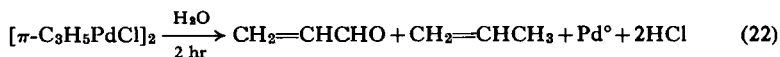
6. The Properties of π -Allyl Transition Metal Complexes

a. Stability. The thermal stability of π -allylic complexes varies from the very stable complexes of palladium, which are often stable above 200°C, to the very unstable and incompletely characterized tris(π -allyl) complexes of chromium and iron. Most π -allylic complexes are oxidized by atmospheric oxygen, especially in solution. An extreme example is bis(π -allyl)nickel which spontaneously ignites in air. However, many π -allylic complexes only show decomposition in air after several hours exposure.

Many π -allylic complexes are stable to hydrolysis, but others hydrolyze even at room temperature (56).

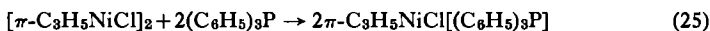


For this reaction, a mechanism involving hydrogen migration via an intermediate complex with an Fe—H bond has been proposed (19). The hydrolysis of bis(π -allyl)palladium chloride has also been shown to proceed readily at room temperature (54, 55), viz.



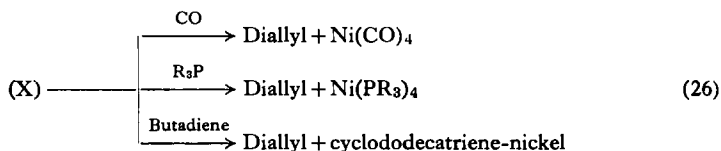
We have already referred to the fact that π -allyl complexes may be formed from olefins and certain metal salts [Eqs. (14a and b)]. Hydrolysis can then afford products similar to those of Eq. (22). It is also known (44) that olefin-palladium complexes themselves hydrolyze, affording the products shown in the model reaction scheme below. Thus, starting from certain transition metal salts it is possible to convert olefins into aldehydes or into ketones.

Similarly, the π -allyl system in the complex $[\pi\text{-C}_3\text{H}_5\text{NiCl}]_2$ is not displaced by triphenylphosphine, but rather the $(\text{NiCl})_2$ bridge is symmetrically cleaved (49).

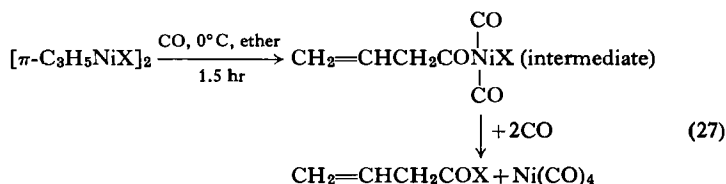


Similar bridge-splitting reactions have been shown for the analogous palladium complexes (94a).

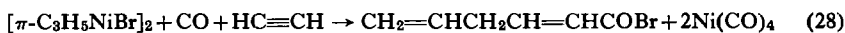
(iii) In contrast to the above results, bis(π -allyl)nickel (X) is very reactive and will readily lose both π -allyl groups, even when treated with olefins (103). See also Section I,B,6c,ii and Chapter I in this volume by Schrauzer.)



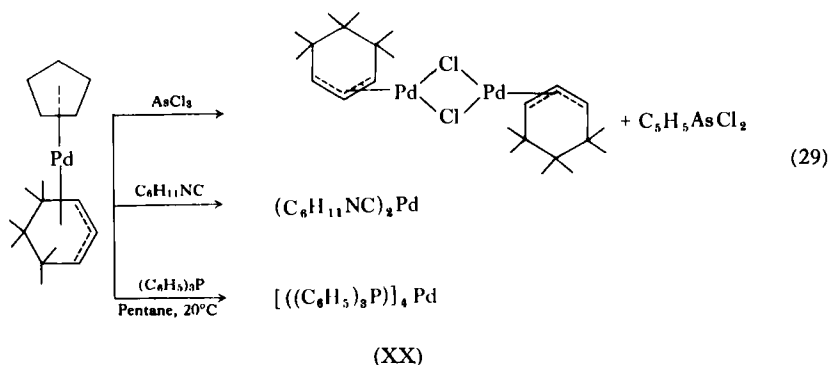
(iv) Reaction of bis(π -allyl)nickel halide dimers with carbon monoxide is more complex than the reaction with triphenylphosphine, the π -allyl system being displaced (25). This reaction has been studied by several workers (10, 23) and the most recent work by Heck (46), in which he resolves some earlier anomalies, suggests the following reaction sequence.



Analogous studies on some palladium complexes have been noted (74a). A similar reaction with a mixture of carbon monoxide and acetylene has also been studied (46).



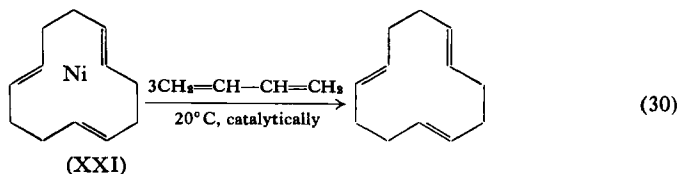
(v) The complex $\pi\text{-C}_5\text{H}_5\text{Pd}(\pi\text{-C}_6\text{H}_9)(\text{XX})$ undergoes reaction with donor ligands similar to those of the nickel compound (X) [Eq. (26)] (29).



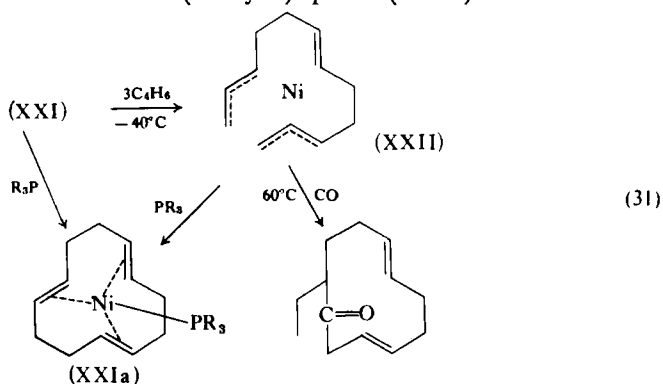
From the reaction with arsenic trichloride it appears that the cyclopentadienyl group is more readily displaced from the metal than the π -allylic system. In contrast, however, oxidation in the presence of hydrogen chloride of π -C₅H₅Mo(CO)₂(π -C₃H₅) affords the dioxochloro complex π -C₅H₅MoO₂Cl (14). Thus, in this case it is the π -allyl group which has been displaced from the metal. From these results and comments, therefore, it seems that the stability and reactivity of π -allyl complexes varies widely from metal to metal, and also depends on the nature of the other ligands attached to the metal.

c. The Catalytic Properties of Some π -Allylnickel Complexes. Some of the most exciting and elegant work in the field of π -allylic and π -olefin-transition metal complexes has recently been carried out by Wilke and his co-workers. This work, which underlines the importance and promise of organometallic compounds as homogeneous catalysts, has been reviewed by Wilke (103), and by Schrauzer (see Chapter I). Here only a few examples are given so as to indicate the nature and extent of the work and more particularly its relationship with other π -allyl metal complexes reviewed in this chapter.

(i) The 16-electron complex cyclododecatrienyl-nickel (XXI) reacts catalytically with butadiene at 20° C. The diene undergoes cyclotrimerization and *cis* and *trans* isomers of cyclododecatriene are formed. The cyclododecatriene ligand so readily "slips off" the nickel that Wilke refers to (XXI) as "bare" nickel.

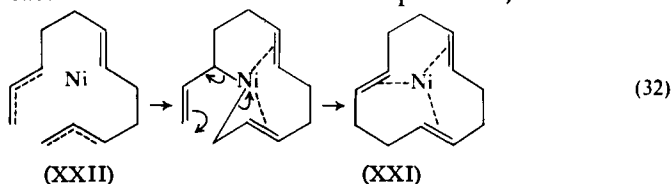


(ii) If the above reaction is carried out at -40°C then only three molecules of butadiene are absorbed per molecule of cyclododecatriene-nickel and a complex formulated as a bis(π -allylic) species (XXII) is formed.

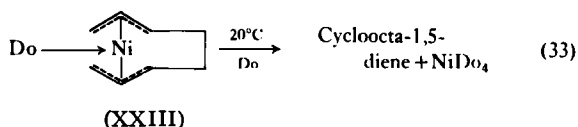


Some further reactions of (XXII) providing additional evidence for its formulation, are also shown.

(iii) Further support for the formulation of (XXII) comes from the observation that bis(π -allyl)nickel (X) will also react catalytically with butadiene to form cyclododecatriene-nickel [Eq. (26)]. Cyclization of the bis(π -allylic) complex (XXII) to the cyclododecatriene complex (XXIa) may be compared with the formation of diallyl from bis(π -allyl)nickel. Both reactions proceed thermally but preferably under the influence of electron donors. Wilke represents these reactions as internal electron shift processes,

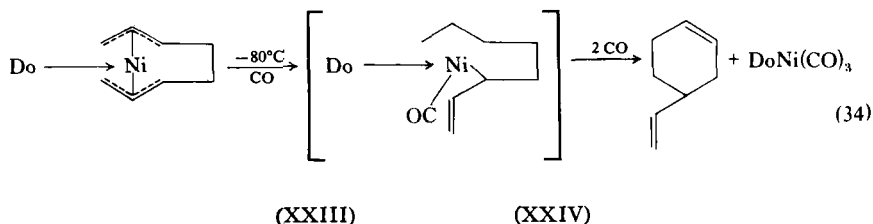


(iv) A cyclodimerization reaction of butadiene to cycloocta-1,5-diene involving intermediate π -allylic complexes may be achieved if the nickel catalyst has a coordination position blocked by a strongly complexing ligand. An 18-electron intermediate such as (XXIII) is proposed; it has actually been isolated when Do = tris(2-biphenyl)phosphite.



(XXIII)

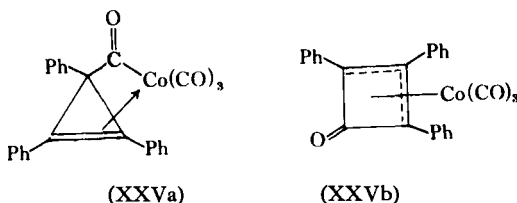
Interestingly, treatment of (XXIII) with carbon monoxide results in a slightly different reaction with formation of vinylcyclohexene rather than cycloocta-1,5-diene. It is suggested that the reaction involves partial displacement by carbon monoxide of one of the π -allylic groups to afford an intermediate σ -allyl system (XXIV).



Wilke and his co-workers have studied many other analogous reactions and have observed catalytic cyclization with a number of other systems. There is no doubt that this elegant study will provide the impetus and the inspiration for a renewed attack on the field of transition metal homogeneous catalysis.

7. Some Miscellaneous Complexes

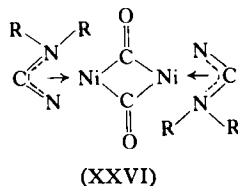
a. π -Cyclopropenyl Complexes. Attempts to prepare π -cyclopropenyl systems have been reported (8a, 12, 69). Although there seems no clear reason why such complexes should not exist, the attempted syntheses have so far been unsuccessful. The reaction between triphenylcyclopropenyl halides and sodium cobalt tetracarbonyl affords a complex for which structures (XXVa and b) have been proposed (12, 5).



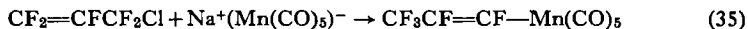
In a recent note, brick-red crystals prepared from triphenylpropenyl halides and nickel tetracarbonyl are tentatively suggested to be μ -halogeno-bis- π -triphenylpropenyldinickel dicarbonyl (42a).

b. Dialkylcyanamide Complexes. The reaction between nickel carbonyl and dialkyl cyanamides gives rise to dimeric complexes for which structure

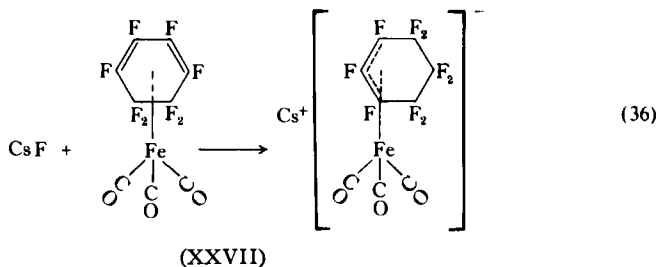
(XXVI) has been proposed (5). Evidence for the structure comes mainly from infrared studies, and is thus not unequivocal.



c. *π -Perfluoroallyl Metal Complex.* There have been attempts to prepare a π -perfluoroallyl metal system. The reaction between perfluoroallyl chloride and sodium manganese pentacarbonyl results in rearrangement of the allyl to a propenyl group (71, 78).



A similar reaction occurs with the salt $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$. A π -perfluorocyclohexenyliron complex (XXVII) has, however, been prepared by a novel fluoride addition reaction (91).



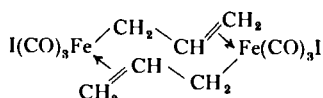
For a discussion of these and related fluorocarbon complexes of transition metals the reader is referred to the chapter by Treichel and Stone in Volume I of this series.

d. X-ray studies on an unusual and complicated binuclear phenylacetyleneiron carbonyl complex $(\text{C}_6\text{H}_5\text{C}_2\text{H})_3\text{Fe}_2(\text{CO})_6$, (53) have shown that part of the bonding of the hydrocarbon system to an iron atom may be described in terms of a π -allylic bond (67).

C. μ -Allyl Metal Complexes

The reaction between allyl halides and iron carbonyls has been studied (83, 93) and there is some difference between the reported nature of the

products. From the reaction between allyl halides and iron enneacarbonyl Murdoch and Weiss (83) obtained complexes which they formulated as $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{X}$, where X = Cl, Br, or I. Plowman and Stone (93) studied the reaction of allyl halides with iron pentacarbonyl and were only able to isolate an allyliron complex of formula $\text{C}_3\text{H}_5\text{Fe(CO)}_3\text{I}$. On the basis of molecular weight determinations in cyclohexane and proton magnetic resonance studies the latter workers suggested that this complex in solution exists in a monomer-dimer equilibrium. It was suggested that the dimeric species involves bridging allyl groups (XVIII).



In view of the occasional unreliability of molecular weight determinations and fickle anomalies of proton magnetic resonance data it is not yet certain that a μ -allyl system has been found, although such complexes are perfectly plausible. Murdoch and Weiss do not report either molecular weight or proton magnetic resonance data.⁵

II

CLASSIFICATION OF THE COMPLEXES AND SPECULATIONS ON THE EXISTENCE OF OTHERS

Allyl complexes form a part of the series of π organometallic complexes classified by the number of electrons the ligand formally contributes to the ligand-metal bond (see Table V).

A π -allyl metal complex may also be classified in terms of the other ligands attached to the metal, be they other allyl groups or different groups entirely.

TABLE V

CLASSIFICATION OF COMPLEXES BY ELECTRONS CONTRIBUTED BY LIGAND

Number of electrons	Name of class	Example of Ligand
2	Alkene	Ethylene
3	Allylic	π -Allyl
4	Diene	Cyclobutadiene, butadiene
5	Dienyl	π -Cyclopentadienyl
6	Triene	Benzene, cycloheptatriene
7	Trienyl	π -Cycloheptatrienyl

⁵ Some recent independent studies (49a) support the observations of Plowman and Stone.

TABLE VI. CLASSIFICATION OF π -ALLYL METAL COMPLEXES

Ligands	Ti	V	Cr
Bis(π -allyl)	—	$(\pi\text{-C}_3\text{H}_5)_2\text{V}$	$(\pi\text{-C}_3\text{H}_5)_2\text{Cr}$
Tris- and tetra(π -allyl)	$(\pi\text{-C}_3\text{H}_5)_4\text{Ti}$	$(\pi\text{-C}_3\text{H}_5)_3\text{V}$	$(\pi\text{-C}_3\text{H}_5)_3\text{Cr}^*$
π -Allyl carbonyl ^c }	—	—	$[\pi\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_4]^-$
	—	—	$(\pi\text{-C}_3\text{H}_5)_2\text{Cr}(\text{CO})_3$
	—	—	—
π -Allyl cyclopentadienyl	$(\text{C}_5\text{H}_5)\text{Ti}(\pi\text{-C}_3\text{H}_5)$	$\text{C}_5\text{H}_5\text{V}(\pi\text{-C}_3\text{H}_5)_2$	$[\text{C}_5\text{H}_5\text{Cr}(\pi\text{-C}_3\text{H}_5)_2]_2$
π -Allyl cyclopentadienyl carbonyl	—	$\text{C}_5\text{H}_5\text{VCO}(\pi\text{-C}_3\text{H}_5)_2$	$\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\pi\text{-C}_3\text{H}_5^\dagger$
π -Allyl halides ^d	$(\pi\text{-C}_3\text{H}_5)_2\text{TiX}_2$	—	—
π -Allyl carbonyl halides ^{c,d}	—	—	—
π -Allyl cyclopentadienyl halides ^d	—	—	$\text{C}_5\text{H}_5\text{Cr}(\pi\text{-C}_3\text{H}_5)_2\text{X}$
π -Allyl cyclopentadienyl carbonyl halides ^{c,d}	—	—	—

^a Those complexes which have been reported are marked with an asterisk, whereas those complexes for which there are substituted analogs known are marked with a dagger.

^b There is some evidence that these complexes or their derivatives exist.

This has been done in the first column of Table VI. In this table known π -allyl metal compounds are marked with an asterisk. Also included and marked with a dagger are some complexes, not known themselves but whose substituted π -allyl derivatives have been isolated. Using these examples, and in the light of the rare gas formalism and consideration of other known organometallic complexes, possible complexes of the first-row transition metals, which are not known but which might be expected to exist, are formulated. We have indulged in this speculation in order to show the various possible types and future scope of π -allyl metal complex chemistry.

III

SOME RECENT WORK ON ALLYL COMPLEXES OF THE MAIN GROUP METALS

In the field of alkali metal organic derivatives, the study of allyl compounds is a comparatively recent development. Alkenylsodium and potassium deri-

AND SPECULATION ON THE POSSIBLE EXISTENCE OF OTHERS^a

Mn	Fe	Co	Ni
$(\pi\text{-C}_3\text{H}_5)_2\text{Mn}$	$(\pi\text{-C}_3\text{H}_5)_2\text{Fe}$	$(\pi\text{-C}_3\text{H}_5)_2\text{Co}$	$(\pi\text{-C}_3\text{H}_5)_2\text{Ni}^*$
$(\pi\text{-C}_3\text{H}_5)_3\text{Mn}$	$(\pi\text{-C}_3\text{H}_5)_3\text{Fe}^*$	$(\pi\text{-C}_3\text{H}_5)_3\text{Co}$	—
$\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_4^*$	$[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_4]^{+b}$	$\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3^*$	$[\pi\text{-C}_3\text{H}_5\text{Ni}(\text{CO})_3]^{+b}$
$\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_3$	$[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3]^{+*}$	$\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_2^b$	$[\pi\text{-C}_3\text{H}_5\text{Ni}(\text{CO})_2]^{+b}$
$(\pi\text{-C}_3\text{H}_5)_3\text{MnCo}$	$(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$	$[(\pi\text{-C}_3\text{H}_5)_2\text{CoCO}]_2$	$(\pi\text{-C}_3\text{H}_5)_2\text{NiCO}^\dagger$
—	$\text{C}_5\text{H}_5\text{Fe}-\pi\text{-C}_3\text{H}_5$	$[\text{C}_5\text{H}_5\text{Co}-\pi\text{-C}_3\text{H}_5]^+$	$\pi\text{-C}_5\text{H}_5\text{Ni}-\pi\text{-C}_3\text{H}_5^*$
—	$\text{C}_5\text{H}_5\text{FeCO}-\pi\text{-C}_3\text{H}_5^*$	$[\text{C}_5\text{H}_5\text{CoCO}-\pi\text{-C}_3\text{H}_5]^{+*}$	—
—	$[(\pi\text{-C}_3\text{H}_5)_2\text{FeX}]_2$	$[(\pi\text{-C}_3\text{H}_5)_2\text{CoX}]_2$	$[\pi\text{-C}_3\text{H}_5\text{NiX}]_2^{*e}$
$\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_2\text{X}]_2$	$\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}^*$	$(\pi\text{-C}_3\text{H}_5)_2\text{CoCOX}^\dagger$	$\pi\text{-C}_3\text{H}_5\text{Ni}(\text{CO})_2\text{Cl}$ $\pi\text{-C}_3\text{H}_5\text{Ni}(\text{CO})\text{Cl}^*$
—	$\text{C}_5\text{H}_5\text{Fe}-\pi\text{-C}_3\text{H}_5\text{X}_2$	$\text{C}_5\text{H}_5\text{Co}-\pi\text{-C}_3\text{H}_5\text{X}^*$	—
—	—	$\text{C}_5\text{H}_5\text{CoCO}-\pi\text{-C}_3\text{H}_5\text{X}^\dagger$	—

^c Other donor ligands, such as tertiary phosphines, may or could replace carbon monoxide in these complexes.

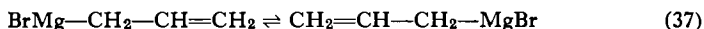
^d Halides may be replaceable by alkyl or aryl groups.

^e $[\pi\text{-C}_3\text{H}_5\text{NiX}_2]^-$ also.

vatives have been prepared by the metallation of an olefin with amylsodium or amylpotassium (66) and several authors have recently reported the preparation of allyllithium (58, 74, 96). A convenient method of preparation is the reaction between phenyl- or butyllithium and tetraallyltin in ether solution (58, 96). The infrared spectrum of allylsodium, studied by Lampher (72), indicates that the salt is derived from a symmetrical ion for which the delocalized structure of the π -allyl system was suggested. The spectrum is similar to that found for π -allyl transition metal complexes. The lowering of the skeletal stretching frequency from its value in the free double bond (approx. 1600 cm^{-1}) to 1535 cm^{-1} is consistent with the molecular orbital description of the allyl negative ion (6). It may be noted that the infrared spectra of alkenylsodium complexes indicate the presence of isomers which may be considered analogous to the *syn* and *anti* isomers of π -methylallyl-cobalt tricarbonyl (Section I,B,4,d).

The proton magnetic resonance spectra of allyllithium and allylmagnesium halides (58, 85, 86) however, can be satisfactorily interpreted on the basis of an AX_4 system. This means that the four terminal protons of the

allyl group attain magnetic equivalence, implying rapid intramolecular or intermolecular exchange processes. It has been suggested that a fast allylic rearrangement takes place where the covalent structures have sufficiently long lifetimes to permit free internal rotation of the methylene groups (85, 86).



Structures involving a symmetrical π -allylmagnesium or lithium arrangement are considered unlikely on the basis of these proton magnetic resonance studies (58, 85, 86). Similar magnetic resonance studies on butenylmagnesium bromide indicate that in solution the butenyl Grignard reagent is largely, possibly exclusively, in the form of the crotyl isomer, $\text{CH}_3\text{CH}=\text{CH}_2-\text{CH}_2\text{MgBr}$ (87).

The spectra and the general properties of the lithium and magnesium allyl complexes indicate that they are essentially covalent compounds. However, in contrast, the sodium and potassium allyl complexes appear to be essentially salts.

References to other allyl metal complexes are given in Table VII and they are not discussed further.

TABLE VII
REFERENCES TO SOME ALLYL MAIN GROUP METAL COMPLEXES

Metal	Reference	Metal	Reference	Metal	Reference
Be	—	B	(11)		
Mg	(105)	Al	(106)	Si	(18)
Ca	—	Ga	—	Ge	(11)
Sr	—	In	—	Sn	(57, 84)
Ba	—	Tl	—	Pb	(35, 73)

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Synthesis of Cyclopentadienyl Metal Compounds

JOHN M. BIRMINGHAM

Arapahoe Chemicals, Inc.
Boulder, Colorado

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I

INTRODUCTION

A new field of organometallic chemistry was introduced in 1951 by the discovery of ferrocene. This independent discovery by Kealy and Pauson (1) and Miller *et al.* (2) stimulated intensive research in the field of cyclopentadienyl metal chemistry and led to the synthesis of several hundred compounds. Many more new compounds may be expected in the future.

Two general approaches have been applied to the synthesis of cyclopentadienyl metal compounds: direct formation of cyclopentadienyl-metal bonds; and transformation of cyclopentadienyl metal compounds to other related compounds. The first of these approaches encompasses methods of synthesis for most of the basic classes of cyclopentadienyl metal compounds and is the principal subject of this review. Methods for transforming one cyclopentadienyl metal compound into another are mentioned only in outline.

The final section is a tabular survey of cyclopentadienyl metal compounds and the methods by which they have been prepared. Yield, melting point, and color are also included. Compounds synthesized by substitution of

various groups into the cyclopentadienyl rings of ferrocene are not included.

A special nomenclature for the cyclopentadienyl metal compounds has grown up because of the complexity of their chemical names. The dicyclopentadienyl metal compounds, $(C_5H_5)_2M$, are called ferrocene, cobaltocene, vanadocene, ruthenocene, etc., and these names will be used in this review. Furthermore, the abbreviation Cp will be used to represent C_5H_5 , the cyclopentadienyl radical.

II

SYNTHESIS BY DIRECT FORMATION OF CYCLOPENTADIENYL—METAL BONDS

Cyclopentadienyl—metal bonds may be synthesized by direct reaction of cyclopentadiene with certain metals and their compounds or by reaction of ionic metal cyclopentadienides with compounds of metals wherein cyclopentadienide anion displaces a ligand bonded to the metal. These bonds may also be formed in a limited number of instances by reaction of alkenes or alkynes with metal compounds.

Synthesis of cyclopentadienyl compounds of metals from cyclopentadiene depends on the strongly acidic properties of cyclopentadiene. This acidity may be attributed to the ready formation of the highly resonance-stabilized cyclopentadienide anion, $C_5H_5^-$, in which there are six delocalized π electrons. This method is limited primarily to the active metals of Groups IA and IIA and to their strongly basic compounds. The compounds produced are principally the ionically bonded metal cyclopentadienides.

The reaction of the ionic cyclopentadienides with metal compounds is by far the most general method for synthesis of cyclopentadienyl metal compounds. This method is applicable both to transition metals, which form π -bonded cyclopentadienyl compounds principally, and to main group metals which form σ -bonded cyclopentadienyl compounds.

The classification of synthetic methods adopted here, based on whether cyclopentadiene or the cyclopentadienide anion is the reacting species, is somewhat arbitrary and may not be mechanistically correct in all cases. It is probable that in many of its reactions cyclopentadiene undergoes partial ionization and that the reacting species may actually be cyclopentadienide anion.

A. From Cyclopentadiene

The strong acidity of cyclopentadiene, estimated as approximately $pK_a = 17$ (3), was first recognized by Thiele, who took advantage of this property in the preparation of potassium cyclopentadienide from potassium metal and cyclopentadiene (4). While direct reaction with cyclopentadiene is limited in scope to the elements of Groups IA and IIA, to their strongly basic compounds, and to a few other elements, it is the only approach for the synthesis of the ionic cyclopentadienides of elements of Groups IA and IIA. Direct reaction of cyclopentadiene is also applicable to the preparation of certain compounds of the $(C_5H_5)_nM(CO)_x$ class from metal carbonyls and is often the preferred method.

Syntheses of cyclopentadienyl metal compounds from cyclopentadiene are carried out under widely varying conditions depending on the properties of the metallic reactants. These reactions may be carried out in the vapor phase at temperatures as high as 600° C or they may be carried out in the liquid phase in the presence of a solvent at 25° C. The cyclopentadienyl metal compounds produced are isolated either by sublimation, if the reaction has been run in the vapor phase, or by crystallization, if the compound has been formed in solution. If the compound is to be used as an intermediate in a subsequent synthesis, then it is not usually isolated in pure form, but is used in solution in a suitable solvent of high dielectric constant or as a slurry in a hydrocarbon solvent.

Nearly all synthetic methods for cyclopentadienyl metal compounds require first the preparation of cyclopentadiene from dicyclopentadiene. This is accomplished by thermal depolymerization of dicyclopentadiene at temperatures above 180° C. Because cyclopentadiene is unstable at room temperature it must be stored at low temperatures to prevent dimerization to dicyclopentadiene. The rate of dimerization is about 0.05% per hour at -20° C and 1% per hour at 10° C (5).

a. *Preparation of Cyclopentadiene from Dicyclopentadiene.* A convenient laboratory apparatus for the depolymerization of cyclopentadiene is shown in Fig. 1. Any solvent boiling between 180° and 350° C which does not react with cyclopentadiene is satisfactory as a heat transfer medium for the depolymerization process. Dicyclopentadiene is added to the refluxing solvent at a rate of 100–300 ml/hr. Depolymerization is nearly instantaneous and the vapors pass through the first condenser and are condensed in the second condenser. Cyclopentadiene is collected in a receiver cooled with ice. The first condenser prevents contamination of the cyclopentadiene with solvent

by condensing the solvent and returning it to the flask. Yield is 95% of the theoretical value.

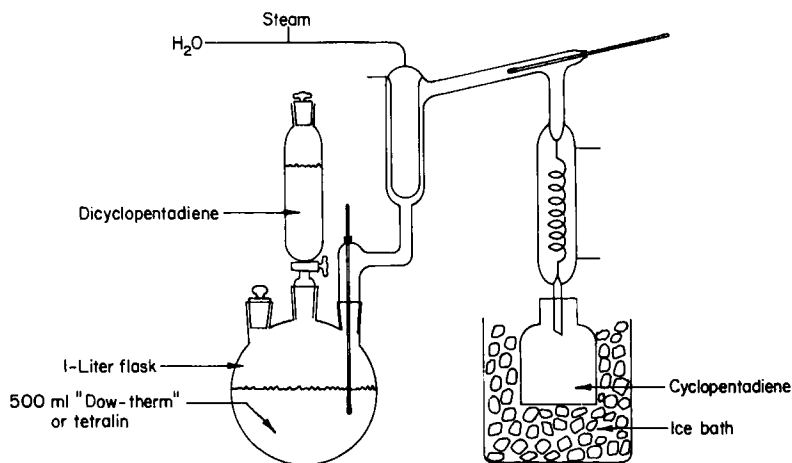


FIG. 1. Apparatus for depolymerization of cyclopentadiene.

1. *Reaction of Cyclopentadiene with Metals (Method 1)*

Direct reaction of metals with cyclopentadiene may be represented by the general equation:



While this is the simplest method for preparing metal cyclopentadienyl compounds, it is one of the least general. It is limited to the elements Li, Na, K, Ca, and Sr and under rather vigorous conditions of temperature to Mg, In, Tl, and Fe. The reaction is usually carried out in the liquid phase at 25° to 100° C in the presence of a solvent for lithium, sodium, and potassium, or in the vapor phase at 400°–600°C for the less reactive elements. Usually the cyclopentadienides of lithium, sodium, and potassium are not isolated but are used in solution as intermediates for the preparation of other cyclopentadienyl metal compounds. Compounds produced by reaction of cyclopentadiene vapor with metal are usually sufficiently volatile to sublime away from the reaction zone and condense in the cooler portion of the apparatus.

Potassium is sufficiently active to react with cyclopentadiene when cyclopentadiene is added to a suspension of potassium shot in toluene (4). Sodium fails to react with cyclopentadiene under similar conditions. When, however,

sodium is dispersed to particles 1–3 μ in diameter, reaction with cyclopentadiene proceeds in xylene at moderate rate at 25° C in 95% yield (6).

As might be expected, alkali metals react with cyclopentadiene much more readily in a solvent in which the alkali metal cyclopentadienide has some solubility. Fischer and Jira (7–9) first used liquid ammonia as a solvent for this reaction and obtained high yields of the ionic cyclopentadienides of Li, Na, and K. It is interesting that the reaction of sodium with cyclopentadiene in liquid ammonia does not produce hydrogen, but yields cyclopentene according to the stoichiometry of the following equation (10, 11)



Wilkinson *et al.* (12, 13) found tetrahydrofuran and 1,2-dimethoxyethane to be most convenient and versatile solvents for the reaction of alkali metals with cyclopentadienes. Sodium cyclopentadienide is generally formed in greater than 95% yields in tetrahydrofuran (THF) and only a few per cent of by-product cyclopentene is formed. Other solvents which have been used are diethyl ether (14), xylene, *tert*-butanol (15), and diethyl ether–xylene mixtures (16). A systematic study of the effect of solvent on yield in the reaction of Li, Na, and K with fluorene indicated that yield decreased in the order 1,2-dimethoxyethane > diethyl ether, \approx THF > dioxane > diethyl ether (17). In general, however, sodium cyclopentadienide in tetrahydrofuran has been the most widely used reagent for the preparation of other cyclopentadienyl metal compounds. (See Section II,A,1a; representative experimental methods are collected at the end of each section.)

Reaction of cyclopentadiene vapor with metal at high temperature was the method used by Miller *et al.* (2) for one of the two original preparations of ferrocene. Iron for this reaction was prepared by reduction of Fe_2O_3 with hydrogen. Yields of ferrocene were low and the reaction continued at 300° C for only a few minutes before it stopped and it was necessary to reactivate the iron with hydrogen. Yields are improved slightly by adding molybdenum to the iron mixture. Others (19) have studied this method and have obtained yields of 20–40% by the passage of a mixture of cyclopentadiene and hydrogen over Fe_2O_3 .

Magnesium reacts with cyclopentadiene vapor very readily at 500° C and gives magnesium dicyclopentadienide in excellent yield (20). This is the preferred method for the preparation of this compound. Other elements which react directly with cyclopentadiene are indium, at 460°–580° C and 3–4 atm pressure, and thallium, at 440°–470° C and 2–3 atm pressure (21).

Thallium cyclopentadienide is, however, more conveniently prepared by the reaction of thallium hydroxide with cyclopentadiene, a procedure which will be described under Method 2.

Substituted cyclopentadienes also form metallic derivatives by direct reaction in the liquid phase with elemental lithium, sodium, and potassium. Thus, indene reacts with sodium to form sodium indenide (11, 23, 24) and lithium, sodium, and potassium react with fluorene (17, 25). Reaction of metals with substituted cyclopentadienes in the vapor phase has not been extended beyond methylcyclopentadiene.

a. *Preparation of Sodium Cyclopentadienide.* [Modification of *Organic Syntheses* procedure, (18)]. A 500-ml three-neck flask is fitted with a mechanical stirrer, a 125-ml addition funnel, and a reflux condenser topped with a nitrogen inlet tube which is connected through a T-joint to a nitrogen supply and a xylene-filled bubbler. In the flask are placed 125 ml of sodium-dried xylene, 11.5 gm (0.5 gram atom) of sodium, and 0.11 gm of aluminium monostearate. The mixture is heated above 105° C, and the sodium is finely dispersed by rapid stirring. Stirring is stopped and the mixture is cooled rapidly to 25° C under nitrogen. The cooled mixture is allowed to settle, the bulk of the xylene is decanted, and tetrahydrofuran (156 ml) is added to the finely divided sodium suspension. During a period of 1 hr a mixture of 44 ml (0.525 mole) of cyclopentadiene and 44 ml of tetrahydrofuran is added while the temperature is kept between 30° and 40° C by external cooling. Stirring is continued for 2 hr at 30°–40° C, after which only a trace of sodium remains unreacted. The yield is nearly quantitative based on sodium.

b. *Preparation of (C₅H₅)₂Mg (22).* Nitrogen flowing at the rate of 275 to 300 ml/min is saturated with cyclopentadiene by passing the gas through a bubbler containing cyclopentadiene. This gaseous mixture is passed downward through a vertical Pyrex tube 1½ inches O.D. which is heated electrically to 500°–600° C. Magnesium metal turnings are supported in the furnace tube by a circle of nichrome gauze held in place by a constriction in the tube. The product, which falls from the furnace as a white solid, is collected in a nitrogen-blanketed receiver at the bottom of the tube. Unreacted cyclopentadiene is collected in a dry ice–ethanol trap. Yields above 80%, based on the cyclopentadiene consumed, have been obtained.

2. Reaction of Cyclopentadiene with Basic Metal Compounds (Method 2)

The general equation for the reaction of basic metal compounds with cyclopentadiene is



This method is applicable to the strongly basic compounds of alkalis and alkaline earths and of Tl, Fe, Co, Ni, Cu, and Pd. It is the preferred method for preparing CpTl and CpPdCl and is a novel method for CpK. Metal compounds which have been used are in the form of hydroxides, hydrides, acetylides, alkoxides, oxalates, oxides, and acetates. Organometallic derivatives of very weakly acidic hydrocarbons, such as Grignard reagent, butyllithium, and phenyllithium, are also included. This method has been used primarily for the preparation of cyclopentadiene derivatives, although derivatives of methyl cyclopentadiene, indene, and fluorene have also been prepared. The Grignard reagent, CpMgX, is generally prepared by reaction of cyclopentadiene with an alkyl Grignard reagent.

Although this reaction may be carried out either in the presence of an organic solvent of high dielectric constant or in the vapor phase at elevated temperature, substantially higher yields usually result when a solvent is used. Even water may be used as a solvent for preparation of thallium and potassium cyclopentadienides.

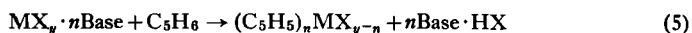
The synthesis of ionic cyclopentadienides of thallium and potassium in aqueous solution is somewhat surprising in view of the much greater acidity of water compared to cyclopentadiene. The presence, however, of a small concentration of cyclopentadienide anions in basic aqueous solution has been detected by UV spectrophotometry (26). The extreme insolubility of thallium cyclopentadienide presumably is sufficient to permit its nearly quantitative precipitation from 1 M potassium hydroxide solution (27–29). Greater solubility and ease of hydrolysis of potassium cyclopentadienide requires the use of saturated potassium hydroxide for its preparation (30). Potassium cyclopentadienide prepared in this manner is a white, air-sensitive precipitate with a curdy appearance.

Riemschneider and Helm (31) have investigated the reaction of ferrous oxalate with cyclopentadiene vapor at 300°–400° C. They found that ferrous oxalate does not react directly with cyclopentadiene but is reduced to metallic iron which then reacts with cyclopentadiene to form ferrocene. Thus, it is probably similar to the reaction described in Method 1 (2).

The only method for the preparation of a cyclopentadienyl derivative of copper is the reaction of cupric oxide with cyclopentadiene in the presence of triethylphosphine. The product of this reaction is CpCu · PEt₃ (32). Attempts to prepare CpCu by reaction of cuprous halides with cyclopentadiene in the presence of base, or with CpNa or CpMgBr have failed (32).

By suitable modification, the direct reaction of cyclopentadiene may be

applied even to acidic or neutral salts of those elements which do not readily form stable basic salts. This is accomplished by inclusion of a base in the reaction mixture. Thus, either a basic complex salt or a simple basic salt is formed.



Bases with a dissociation constant greater than 1×10^{-5} , such as diethylamine, triethylamine, piperidine, ammonia under pressure, and sodium alcoholate, have been used (33-35). Salts of Ni, Co, Fe, Ti, Zr, and Hg react in this manner. Although this reaction is limited in scope to a few elements, it does give high yields of those compounds which can be prepared.

In the usual experimental procedure, an acidic salt is first complexed with base and then treated with cyclopentadiene which reacts to form the cyclopentadienyl metal compound. The by-product salt is separated from the cyclopentadienyl metal compound by extraction with water.

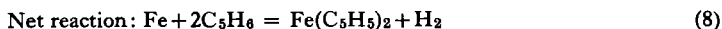
Synthesis of cyclopentadienyl metal compounds from basic metal salts derived from a base and a neutral or acidic metal salt is limited primarily to cyclopentadiene and in a few instances methylcyclopentadiene (37). The use of other substituted cyclopentadienes has not been reported and it is probable that only the very strongest bases would be effective in promoting their reaction.

Solvents of high dielectric constant with good solvent properties for the reacting basic metal salt are most satisfactory media for the reaction of cyclopentadiene with metal salts in the presence of base. Most frequently used solvents are tetrahydrofuran and 1,2-dimethoxyethane; less frequently used solvents are dioxane, ethanol, ammonia, and diethylamine.

In the initial description of this method triethylamine, diethylamine, pyridine, and sodium ethylate were reported to be effective, but yields of ferrocene and titanocene dichloride were only 3-4% (33). These low yields probably resulted from the use of unreactive ferrous chloride prepared by high temperature dehydration.

Synthesis of ferrocene in high yield by this method has been reported by a number of investigators (18, 34-36, 38). Wilkinson *et al.* (36) have described the preparation of ferrocene, and dicyclopentadienyl compounds of cobalt and nickel in yields of 80-90%; anhydrous diethylamine served both as solvent and acceptor for hydrogen halide. This procedure for preparing ferrocene has been published in detail in *Organic Synthesis* (18).

A potentially low-cost synthesis of ferrocene based on this method has been devised by Pruett and Morehouse (35, 39). If the by-product amine hydrochloride is recycled, a process which utilizes only iron and cyclopentadiene results. This sequence is:



a. *Preparation of Thallium Cyclopentadienide* (27). To a solution of 25 gm of thallium sulfate and 10 gm of potassium hydroxide in 200 ml of water at 25°C is added 5 gm of cyclopentadiene. After stirring the mixture for a few minutes the precipitate of thallium cyclopentadienide is washed with ice water and cold methanol and then dried. Yield is 19.5 gm of CpTl (95% of theoretical yield based on cyclopentadiene).

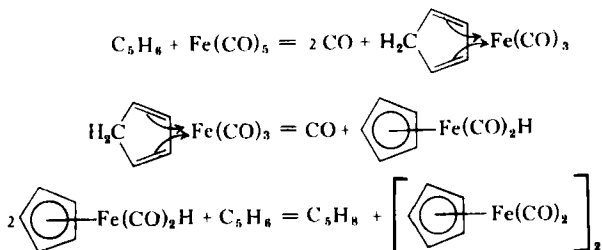
b. *Preparation of Dicyclopentadienyltitanium Dichloride*. (Based on ref. 36.) To 300 ml of tetrahydrofuran is added 60 gm (0.24 mole) of titanium tetrachloride with good mixing and cooling. To this mixture is added 100 ml (1 mole) of diethylamine followed by 120 ml (1.4 mole) of cyclopentadiene. The reaction mixture is refluxed (60°–65° C) for 8 hr, cooled to 5° C, and filtered. The precipitate which is a mixture of Cp_2TiCl_2 and diethylamine hydrochloride is washed with tetrahydrofuran, and petroleum ether (30°–60° C boiling range) and dried in air. The precipitate is added to 200 ml of 4 N hydrochloric acid, and the resulting slurry is stirred for 10 min and filtered. The red Cp_2TiCl_2 is washed with ice water and methanol and then dried. Yield is 45–48 gm (75–80% of theory), m.p. is 287°–289° C with slight decomposition.

3. Reaction of Cyclopentadienes with Metal Carbonyls (Method 3)

Cyclopentadiene reacts directly with metal carbonyls to form two classes of compounds, each with cyclopentadienyl–metal bonds. Under mild conditions cyclopentadienyl metal carbonyls, $\text{C}_5\text{H}_5\text{M}(\text{CO})_x$, are formed, and this is the preferred method for preparing many of them. Under more vigorous conditions dicyclopentadienyl metal compounds, $(\text{C}_5\text{H}_5)_2\text{M}$, are formed. Because, however, yields of dicyclopentadienyl metals are low, this is not an important method for their preparation except possibly in the case of ferrocene (40). This reaction under mild conditions, is carried out in the liquid phase in refluxing dicyclopentadiene. Occasionally, a solvent of high

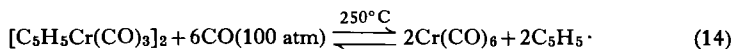
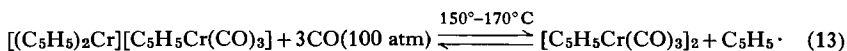
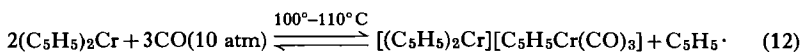
dielectric constant is included if cyclopentadiene itself is used. The product may be isolated by simply filtering the crystals or by subliming the residue after removal of solvent. Under vigorous conditions the reaction is carried out in the vapor phase in a heated tube.

Attachment of one cyclopentadienyl group to iron by reaction of cyclopentadiene with iron pentacarbonyl has been formulated as proceeding through three steps (41).



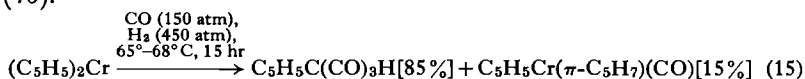
The first step is a simple displacement of two molecules of carbon monoxide. In the second step the acidic hydrogen of π -bonded cyclopentadiene shifts to the iron atom to give π -cyclopentadienyliron dicarbonyl hydride, a known compound. Two molecules of this iron hydride then add hydrogen to cyclopentadiene to form cyclopentene and the dimer of π -cyclopentadienyliron dicarbonyl. This reaction proceeds at temperatures between 150° and 220° C. Above 220° C, the remaining carbon monoxide molecules are displaced by a second molecule of cyclopentadiene forming ferrocene (42).

The reaction of chromium carbonyl with cyclopentadiene at 280°–350° C to form Cp_2Cr (43) is reversible (44, 45).



Carbon monoxide under 100 atm pressure reacts with Cp_2Cr at 100°–110° C to form $[\text{Cp}_2\text{Cr}][\text{CpCr}(\text{CO})_3]$ [reaction (12)] and at 150°–160° C to form $[\text{CpCr}(\text{CO})_3]_2$, [reaction (13)]. At still higher temperatures the remaining ring is displaced and chromium hexacarbonyl is the final product [reaction (14)]. When Cp_2Cr is allowed to react with carbon monoxide (150 atm) in

the presence of hydrogen (50 atm) at 65°–68° C for 15 hr, the major product is $\text{CpCr}(\text{CO})_3\text{H}$ together with 15% of $\pi\text{-C}_5\text{H}_5\text{Cr}(\pi\text{-C}_5\text{H}_7)(\text{CO})_2$ [reaction (15)] (46).

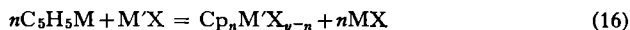


At higher pressures and temperatures the product is predominantly $\text{Cr}(\text{CO})_6$ derived from the decomposition of $\text{CpCr}(\text{CO})_3\text{H}$.

Methylcyclopentadiene readily undergoes reaction with metal carbonyls (47) and even 1,3-diphenylcyclopentadiene reacts with iron carbonyl (48). A novel method for obtaining a ferrocene with one substituted ring, is the reaction of 1,3-diphenylcyclopentadiene with the dimer of cyclopentadienyl-iron dicarbonyl at 170° C to produce 1,3-diphenylferrocene in 15% yield. Other substituted cyclopentadienes which have been used are tetraphenylcyclopentadienone in the preparation of tetraphenyl(hydroxy)cyclopentadienylmanganese tricarbonyl (49) and indene in the preparation of the dimer of indenylmolybdenum tricarbonyl (50). A variety of substituted fulvenes have been used in the preparation of substituted cyclopentadienyl metal tricarbonyl compounds of Cr, Mo, and W (51, 52). This latter reaction proceeds best in the presence of a solvent, such as 1,2-dimethoxyethane, to permit easy abstraction of hydrogen.

B. Reaction of Ionic Cyclopentadienides with Metal Compounds

The reaction of ionically bonded metal cyclopentadienides with metal compounds to form cyclopentadienyl metal compounds may be represented by the general equation



where the metal compound $\text{M}'\text{X}$ is either a metal salt or a metal carbonyl. This is by far the most general method for synthesizing the cyclopentadienyl-metal bond. It is applicable to the preparation of cyclopentadienyl compounds of virtually all of the elements which form these compounds, whether the metals are of transition group or main group type. Ionic cyclopentadienides of Li, Na, and K, as well as the Grignard reagent, CpMgBr , are all suitable reagents for this reaction partially because they are ionized in solvents of high dielectric constant (36). The reactive species is undoubtedly the cyclopentadienide anion, which displaces a ligand from the less reactive

metal compound and forms a cyclopentadienyl derivative of the less reactive metal. A salt of the more active metal M is the metathetical product.

The ionic cyclopentadienide is customarily prepared in advance in the same solvent to be used in the preparation of the cyclopentadienyl metal compound. Stock solutions of reactive cyclopentadienides may be prepared and used as needed. A solution of 2.5 M sodium cyclopentadienide in tetrahydrofuran may be conveniently prepared and stored for this purpose. Since ionic cyclopentadienides are air-sensitive, all reactions must be carried out in an inert atmosphere, usually nitrogen. It is important that the metal compound, usually a chloride or bromide, be anhydrous because the ionic cyclopentadienide reacts preferentially with water.

Reaction of ionic cyclopentadienides with metal compounds does not always proceed according to the stoichiometry of a metathetical reaction. The reason for this is that ionic cyclopentadienides provide a reducing medium and, if the metallic ion of the metal compound is in an easily reducible state, then a portion of ionic cyclopentadienide will be consumed in reducing the metal ion to a lower valence state. When trivalent metal salts are used for the preparation of dicyclopentadienyl metal compounds of the first transition series then at least 3 moles of ionic cyclopentadienide must be used to achieve good yields of the desired dicyclopentadienyl metal compound, the excess beyond 2 moles being necessary to effect reduction of the metal ion to the divalent state. An example of such a reduction is the reaction of ferric chloride with excess sodium cyclopentadienide to form ferrocene. When excess ionic cyclopentadienides are used as reducing agents, unidentified reduction products of cyclopentadiene are formed, usually polymeric in nature, and isolation of the product becomes difficult. Two elements which are not reduced with excess cyclopentadienide ions are Rh and Ir. They give the cation Cp_3M^+ when the metal ion in the $3+$ state reacts with excess cyclopentadienide.

Cyclopentadienyl compounds synthesized by the reaction of ionic cyclopentadienides with metal compounds are usually isolated by evaporating the solvent under vacuum and, if the product is unstable, extracting the dry residue with a hydrocarbon solvent, such as benzene or toluene. Air-sensitive products of sufficient volatility may be sublimed away from nonvolatile residues. When more than gram quantities are required the inconvenience of evaporating to dryness and transferring a pyrophoric residue renders these techniques rather impractical. It is then more convenient to add a hydrocarbon solvent which is less volatile than the reaction solvent and

remove excess ionic cyclopentadienide by hydrolysis. The product may be crystallized from the hydrocarbon solvent. Hydrolytically sensitive products require a solvent in which the product is soluble but excess ionic cyclopentadienide is insoluble.

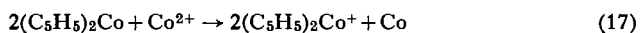
1. *Reaction of Alkali Metal Cyclopentadienides with Metal Salts (Method 4)*

Reaction of alkali metal cyclopentadienides with metal salts has been the most widely used method for the synthesis of cyclopentadienyl metal compounds. Alkali metal cyclopentadienides were first employed in the preparation of cyclopentadienyl metal compounds by Fischer *et al.* (7-9). They used lithium, sodium, and potassium cyclopentadienides in liquid ammonia and obtained complex ammine salts, $M[NH_3]_6(C_5H_5)_2$, which could be decomposed by heating under vacuum to give dicyclopentadienyl compounds of several elements in the first transition series. Wilkinson and Birmingham (13) improved the convenience of the method by using tetrahydrofuran and 1,2-dimethoxyethane as solvents for sodium cyclopentadienide. In these solvents most reactions are rapid and complete, and the reaction may be run conveniently at temperatures between 25° C and reflux. Even the ammine salts, $Ni(NH_3)_6Cl_2$ and $Co(NH_3)_6Cl_2$, react at 30°-40° C with $CpNa$ in THF with complete displacement of ammonia (53). Other solvents which have been used are diethyl ether, *tert*-butanol, *N,N*-dimethylformamide, and a mixture of toluene and ether. Sodium cyclopentadienide is soluble to the extent of 1-2.5 moles/liter in most of these solvents, but is nearly insoluble in toluene and benzene. In those few cases where the solvent reacts with the product it is necessary to prepare the alkali metal cyclopentadienide in one solvent and displace it with another solvent which is compatible with the product. This procedure has been employed in the preparation of Cp_2Zn (54) and Cp_2Pb (15) where sodium cyclopentadienide was prepared in liquid ammonia or *tert*-butanol and these solvents were replaced with *N,N*-dimethylformamide. The influence of solvent is also illustrated in the preparation of tetracyclopentadienyls of Nb, Ta, Mo, W (55), U (56), and Th (57). When excess sodium cyclopentadienide in diethyl ether or benzene reacts with higher halides of the above metals, the tetracyclopentadienyls are produced in good yield. When tetrahydrofuran is substituted for ether or benzene in the above preparations, little if any tetracyclopentadienyl of Nb, W, U, or Th is produced, whereas salts of Mo and W form Cp_2MoH_2 and Cp_2WH_2 (58).

Choice of metal salt is generally governed by a number of factors such as

solubility in the reaction medium, ease of preparation, and lack of reactivity with the product. The metal should preferably be in the same oxidation state as the final cyclopentadienyl metal compound to avoid excessive consumption of alkali metal cyclopentadienide and difficulties in work-up caused by the presence of oxidation products of cyclopentadiene. In liquid ammonia, thiocyanates of cobalt (9), nickel (8), cadmium, etc. have been preferred because of their good solubility, whereas in tetrahydrofuran chlorides and bromides have been most commonly employed. In any case, the selected salt should be anhydrous and may be added either in the dry state or in solution.

The preparation of cobaltocene presents a special problem because the product is partially destroyed through oxidation by cobaltous chloride.



Hexamminecobalt(II) chloride, on the other hand, is not readily reduced by cobaltocene. Hence, its use in place of cobaltous chloride leads to higher yields of cobaltocene (53).

In general, reactions between alkali metal cyclopentadienides and metal salts are carried out at the reflux temperature of the chosen solvent for a period of several hours. However, longer periods of reflux are required for the reaction of certain metal salts. Thus, the preparation of ruthenocene requires several days of refluxing in 1,2-dimethoxyethane to complete the reaction between RuCl_3 and NaCp (59).

Dicyclopentadienylrhenium has not been synthesized, although analogous compounds of the other elements in the manganese group, $(\text{C}_5\text{H}_5)_2\text{Mn}$ and $(\text{C}_5\text{H}_5)_4\text{Tc}_2$, have been prepared. When rhenium pentachloride reacts with excess sodium cyclopentadienide in tetrahydrofuran and the product is isolated by sublimation of the residue after removal of the solvent, the product is a yellow crystalline solid, $(\text{C}_5\text{H}_5)_2\text{ReH}$. This yellow sublimate is accompanied by a slightly more volatile brown oil which has previously been considered as a polymeric organic by-product. This oil is difficult to crystallize but can be made to form brown crystals which may very well be the missing $(\text{C}_5\text{H}_5)_2\text{Re}$. This possibility is strengthened by the observation that addition of sodium borohydride to the reaction mixture prevents the formation of oil (60).

The reaction of alkali metal cyclopentadienides with metal salts is generally applicable to the synthesis of substituted metallocyclopentadienyls. Thus, sodium methylcyclopentadienide readily reacts with metal halides to

form methylcyclopentadienyl metal compounds (47). Similarly, fulvenes may be converted to substituted cyclopentadienide anions, $[C_5H_4CRR'H]$, by sodium (61), $LiAlH_4$, LiR' , or $NaNH_2$ (62, 63). The cyclopentadienide anions thus produced will react with anhydrous ferrous chloride to give high yields of substituted ferrocenes. Azulene has been converted to its anion by lithium alkyls, and then into two stereoisomeric derivatives of ferrocene by reaction with anhydrous $FeCl_2$ (63). Also, azocyclopentadiene has been converted by phenyllithium into phenylazocyclopentadienide and subsequently into phenylazoferrocene (64). Although they have been used principally for ferrocene derivatives, these reactions with substituted cyclopentadienides should be applicable to other elements. Indeed, a derivative of cobaltocene, di(1-hydroxy-3-methyl-cyclopentadienyl)cobalt, has been synthesized from 3-methyl-2-cyclopentadienone, sodium amide, and cobaltous chloride in liquid ammonia (65).

a. *Preparation of Ferrocene (18)*. In a 250-ml three-necked flask, fitted with a mechanical stirrer, a reflux condenser, and an inlet for admission of nitrogen, is placed 100 ml of tetrahydrofuran. With stirring, 27.1 gm (0.166 mole) of anhydrous ferric chloride is added in portions, followed by 4.7 gm (0.084 gram atom) of iron powder. The mixture is heated with stirring under nitrogen at the reflux temperature for 4.5 hr, giving a gray powder with a brown supernatant liquid.

The cooled contents of the 250-ml flask containing ferrous chloride are added to a solution of 0.5 moles of cold sodium cyclopentadienide in 200 ml of tetrahydrofuran (see Method 2 for the preparation of sodium cyclopentadienide) while passing a stream of nitrogen through both flasks. The combined mixture is stirred for 1.25 hr at a temperature just below the reflux temperature. Solvent is removed by distillation, and the ferrocene is extracted from the residue with several portions of refluxing petroleum ether (b.p. 40° – 60° C). The product is obtained by evaporation of the petroleum ether solution. Ferrocene may be purified by recrystallization from pentane or cyclohexane (hexane, benzene, and methanol have also been used) or by sublimation. The yield is 31–34 gm (67–73%), m.p. 173° – 174° C.

b. *Preparation of Cobaltocene (53). Hexamminecobalt(II) Chloride*. A solution of 476 gm of $CoCl_2 \cdot 6H_2O$ (~ 2 moles) is dissolved in 760 gm of water and is heated to 60° C, and during 6 hr about 400 gm of ammonia are added. The solution is cooled with an ice bath and large pinkish-colored crystals of $Co(NH_3)_6Cl_2$ are filtered, washed with ice water, ethanol, and ether. The

product is slightly sensitive to oxidation by air and should be dried under nitrogen or in vacuum. The yield is 360–400 gm (78–86% of theoretical value).

Cobaltocene. To 0.5 mole of sodium cyclopentadienide in 400 ml of tetrahydrofuran (see Method 2 for the preparation of sodium cyclopentadienide) is added 75 gm of $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ and the temperature is raised to 35°–40° C, whereupon ammonia evolution commences. When ammonia evolution is virtually complete, the mixture is refluxed at 65° C for 2 hr. The solvent is removed under vacuum and the dry residue transferred to a sublimation apparatus, where the cobaltocene is isolated in the form of dark violet crystals which are very rapidly oxidized by air. The yield is between 42 and 47 gm (86–96% of theoretical yield based on sodium cyclopentadienide).

An alternative method for isolating the product is to add toluene to the reaction mixture after the reflux period and remove most of the tetrahydrofuran by distillation through a packed column. The mixture is then washed with water to remove salts and residual tetrahydrofuran, and the resulting toluene solution of cobaltocene is dried with anhydrous sodium sulfate.

2. *Reaction of Cyclopentadienyl Grignard Reagent with Metal Salts (Method 5)*

The reaction of cyclopentadienylmagnesium halides with metal salts has been used in the synthesis of many cyclopentadienyl compounds from both transition group and main group elements. One of the two original methods for the synthesis of ferrocene was the reaction of cyclopentadienylmagnesium bromide with ferric chloride (1) and many compounds were prepared by this method during the early period of cyclopentadienyl metal chemistry. With the development of other methods the Grignard method became less favored until now it is seldom employed. One inconvenience of this method is that cyclopentadienylmagnesium halide is not prepared directly but must be prepared by a replacement reaction between cyclopentadiene and a more reactive alkylmagnesium halide. High yields in this replacement reaction are achieved only when diethyl ether is partially replaced by a higher boiling solvent, such as benzene or toluene. Another inconvenience is that it is often necessary to reflux the reaction mixture for 12–24 hr to achieve good yields of cyclopentadienyl metal compounds. When anhydrous halides are used in the preparation of cyclopentadienyl metal compounds from Grignard reagents, yields are often below 50%. Higher yields result with the use of

metal complexes, such as acetylacetonates, which are soluble in organic solvents. The pyridine complex of ferrous chloride, $\text{Fe}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$, gives an almost quantitative yield of ferrocene (42).

The reaction mixture may be worked up in one of two ways. If the product is not hydrolyzable, it may be isolated by hydrolyzing the reaction mixture in dilute mineral acid or ammonium chloride and extracting the product with an organic solvent. In the event that the product is water-sensitive, it may be isolated by sublimation of the dry reaction residue after removal of solvent. Contamination of the product with Cp_2Mg , a sublimable co-product, often occurs. This contaminant may be removed by dissolving the mixture in ether and passing CO_2 into the solution to decompose the Cp_2Mg .

The Grignard method is also applicable to the synthesis of substituted cyclopentadienyl metal compounds. Diindenyliron (66) has been prepared from indenylmagnesium bromide (67) and di(1,3-diphenylcyclopentadienyl)iron from 1,3-diphenylcyclopentadienylmagnesium bromide (68).

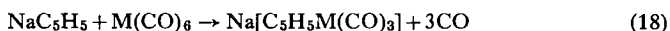
a. *Preparation of Vanadocene* (69). Ethylmagnesium bromide is prepared in the usual way from 8 gm (0.33 mole) of magnesium chips, 36.0 gm (0.33 mole) of $\text{C}_2\text{H}_5\text{Br}$, and 250 ml of absolute diethyl ether. The apparatus used is a 500-ml three-neck flask fitted with a stirrer, reflux condenser, addition funnel, and nitrogen inlet tube. To the Grignard solution is added 24.0 gm (0.36 mole) of cyclopentadiene and the mixture is refluxed for 3 hr or until the evolution of ethylene has stopped. (The rate and yield of this reaction may be improved by displacing part of the ether with benzene and refluxing at the higher temperature, which is attainable in this solvent system.)

To the cyclopentadienylmagnesium bromide solution is added 13.5 gm (0.07 mole) of VCl_4 with cooling. The mixture is refluxed for 8–10 hr, the solvent is removed under vacuum, and the residue sublimed in high vacuum to a temperature of 200°C to give a blue-violet sublimate which is a mixture of Cp_2V and Cp_2Mg . The separation of Cp_2Mg from Cp_2V is effected by dissolving the mixed crystals in 175 ml of nitrogen-saturated ether and passing a stream of CO_2 through the solution. The precipitate of the magnesium salt of cyclopentadienecarboxylic acid is removed by filtration and the precipitate washed with three 24-ml portions of ether. The violet filtrate is concentrated to 20% of its original volume and cooled to -80°C to permit crystallization. The vanadocene is filtered, washed with a small portion of ether, and then resublimed in high vacuum at $80^\circ\text{--}100^\circ\text{C}$ to give 5 gm of violet vanadocene, melting at $167^\circ\text{--}168^\circ\text{C}$. A further 1–2 gm of

product may be isolated from the mother liquor. The yield is 47–55% of the theoretical value.

3. *Reaction of Alkali Metal Cyclopentadienides with Metal Carbonyls (Method 6)*

Displacement of carbon monoxide from metal carbonyls by alkali metal cyclopentadienides is a convenient method for preparing the alkali metal salts of the mixed cyclopentadienyl metal carbonyls. This reaction of carbonyls of Group VIB transition metals is represented by the equation



The salt which is formed may then be treated with acetic acid to yield cyclopentadienyl metal tricarbonyl hydride or with alkyl halides to form alkyl derivatives.

Reaction of sodium cyclopentadienide with the carbonyl halides of noble metals has been useful in the preparation of mixed cyclopentadienyl carbonyls which are usually sublimed directly from the reaction mixture after removal of solvent. In this manner monomeric $\text{CpIr}(\text{CO})_2$ (70), $\text{CpRh}(\text{CO})_2$ (71), $\text{CpIr}(\text{CO})_2$, $[\text{CpRu}(\text{CO})_2]_2$ (72), and $[\text{CpPt}(\text{CO})]_2$ (73) have been synthesized. These reactions are usually carried out under reflux in the solvent which was used to prepare sodium cyclopentadienide.

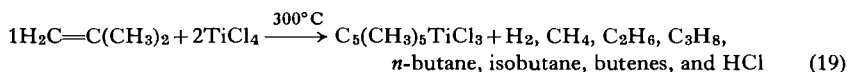
Direct synthesis of mixed cyclopentadienyl carbonyls of certain other transition metals may be accomplished by reaction of metal halide, sodium cyclopentadienide, and carbon monoxide under high pressure (50–300 atm). This reaction probably proceeds via the formation of dicyclopentadienyl metal compound followed by displacement by CO, rather than via formation of metal carbonyl and subsequent displacement by cyclopentadienide anion. An excess of sodium cyclopentadienide is normally used to provide a reducing medium, which is especially important for metals initially in the 4+ or 5+ valence state. Some of the compounds which have been synthesized using this approach are $\text{CpMn}(\text{CO})_3$ (74, 75, 76), $\text{CpRe}(\text{CO})_3$ (77), $\text{Cp}_2\text{Ti}(\text{CO})_2$ (78), $\text{CpTc}(\text{CO})_3$ (79), and $\text{CpNb}(\text{CO})_4$ (80).

C. *From Alkenes and Alkynes*

1. *Reaction of Alkenes and Alkynes with Metal Salts and Metal Carbonyls (Method 7)*

The direct formation of the cyclopentadienyl–metal bond by the reaction of alkenes and alkynes with metal compounds has been applied only to

titanium and manganese. Röhl *et al.* (81) have prepared pentamethylcyclopentadienyltitanium trichloride in 20–30% yields by the reaction of certain olefins with titanium tetrachloride at 300° C and 30–60 atm.



Olefins which undergo this reaction are 1-butene, 2-butene, isobutylene, a mixture of pentene isomers, diisobutylene, and tetrapropylene. Coffield *et al.* (82, 83) have shown that acetylene and manganese pentacarbonyl under 600 psi and at 150° C give 1,2-(propenylene)cyclopentadienylmanganese tricarbonyl. The conditions of this synthesis are similar to those described by Reppe (84) for the reaction of acetylene with other metal carbonyls to form π -bonded complexes.

III

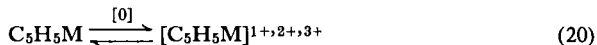
SYNTHESIS BY REACTIONS OF π -BONDED CYCLOPENTADIENYL METAL COMPOUNDS

Syntheses of cyclopentadienyl metal compounds by reactions which do not involve the formation of cyclopentadienyl–metal bonds are not within the scope of this review. However, certain cyclopentadienyl metal compounds are difficult to make by the general methods outlined above, and are best made by converting easily prepared compounds without affecting the cyclopentadienyl–metal bonding. The most important reactions of this sort involve changes in the oxidation state of the central metal atom. Oxidation–reduction methods are therefore discussed in detail. In addition, several other general methods for transforming one cyclopentadienyl metal compound to another are listed with little discussion in order to complete the tabular survey of compounds and methods.

1. Oxidation and Reduction (Method 8)

Synthesis of cyclopentadienyl metal compounds by Methods 1–7 often leads to products in which the metal is in an oxidation state different from that required for a particular purpose. Oxidation or reduction of these compounds is frequently the most convenient method for producing compounds not readily synthesized by direct methods. The general equation for

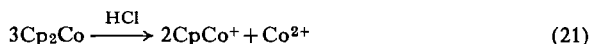
the oxidation of the dicyclopentadienyl compounds of the first transition series may be written as



This reaction is reversible for all elements of this series except cobalt. Oxidation and reduction may be accomplished by anodic or cathodic means or by chemical methods.

All neutral dicyclopentadienyl compounds of the first transition series except ferrocene are oxidized by air and hence must be carefully protected from air during storage. Ferrocene and nickelocene are oxidized to their unipositive cations by 3 *N* nitric acid, whereas vanadocene and cobaltocene are oxidized to their unipositive cations even by 3 *N* hydrochloric acid.

The stoichiometry of the oxidation of cobaltocene by hydrochloric acid is unusual in that, for every three moles of cobaltocene consumed, two moles of $(\text{C}_5\text{H}_5)_2\text{Co}^+$ and one mole of Co^{2+} are produced (31).



This formation of cobaltous ion may, however, be avoided by oxidizing cobaltocene with hydrogen peroxide to give nearly quantitative yields of cobalticinium hydroxide, Cp_2CoOH (8, 85).

Ferricinium salts also are most conveniently prepared by oxidation of ferrocene. Ferric chloride or ceric sulfate will effect this oxidation, as will oxygen passing through acid containing a trace of ferric or cupric ion. In organic media, the oxidation of ferrocene to ferricinium cation may be accomplished by Br_2 in CCl_4 (86), by quinone in benzene (87), or by concentrated sulfuric acid (88).

Dicyclopentadienyl metal cations are soluble in aqueous acid and exhibit properties similar to those of the larger alkaline earth cations. In aqueous solution they are precipitated by large anions, such as picrate, reineckate, tetraphenylborate, hexafluorophosphate, and silicotungstate.

Lithium aluminum hydride in tetrahydrofuran reduced $(\text{Cp})_2\text{VCl}_2$ to $(\text{Cp})_2\text{V}$ (89), whereas the same reagent reduced $(\text{Cp})_2\text{Co}^+$ to CpCoC_5H_6 (90). The ferricinium ion is easily reduced to ferrocene by sodium dithionite, titanous sulfate, or stannous chloride.

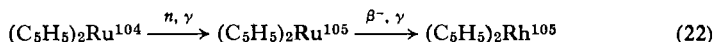
2. Thermal Decomposition (Method 9)

Although ferrocene and many other cyclopentadienyl metal compounds are thermally stable to very high temperatures, two examples of thermal

decomposition are the disproportionation of cyclopentadienylmagnesium bromide (36, 91) to give dicyclopentadienylmagnesium and magnesium bromide and the decomposition of ferricinium ion (48) to give ferrocene.

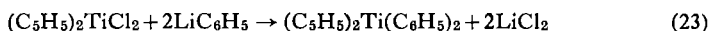
3. Neutron Activation (Method 10)

It is possible in certain cases to produce isotopic modification of cyclopentadienyl metal compounds by neutron activation. An example of this method is the synthesis of $(C_5H_5)_2Rh^{105}$ (92).



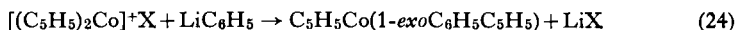
4. Ligand Replacement (Method 11)

Replacement of the cyclopentadienyl ring or of other ligands about the metal atom may be effected by many anionic and neutral species. An example of ligand replacement (93) is



5. Addition Reactions (Method 12)

Addition to the cyclopentadienyl ring or to the metal atom is a frequently used synthetic method, especially for the compounds of Group VIII elements. An example of an addition reaction (94) is



IV

TABULAR SURVEY

A survey of known cyclopentadienyl metal compounds is presented in Table I. This survey is complete through *Chemical Abstracts* index for Volume 58, June 1963, and includes several later references.

Compounds are arranged according to periodic groups starting with the lithium group. Within the compounds of each element the cyclopentadienyl metal compounds, Cp_nM , are listed according to increasing number of cyclopentadienyl groups. When other ligands are present, the compounds are arranged in order of decreasing number of cyclopentadienyl groups. Abbreviations used in addition to Cp are Ind for indenyl, Fluor for fluorenyl, ϕ for phenyl, Me for methyl, and Et for ethyl.

TABLE I
CYCLOPENTADIENYL-METAL COMPOUNDS

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
<i>Lithium Group</i>				
CpLi	dec without melting	Colorless	35	(1), 45, 95; (2), 96, 97
IndLi	dec without melting	Colorless	—	(2), 24
FluorLi	dec without melting	Colorless	31	(1), 17, 95; (2), 95
9-PhenylfluorLi	dec without melting	Colorless	38–85	(2), 98; (1), 95
CpNa	dec 300	Colorless	97	(1), 6, 7, 8, 11, 13, 18, 45, 85, 99–103; (2), 102
IndNa	dec without melting	Colorless	—	(1), 11, 24
FluorNa	dec without melting	Colorless	70–90	(1), 11, 17, 100
CpK	dec without melting	Colorless	87	(1), 4, 7, 9, 45; (2), 30, 104
FluorK	dec without melting	Colorless	70–90	(1), 17, 25
<i>Beryllium Group</i>				
Cp ₂ Be	59–60	Colorless	74	(4), 105
MeCp ₂ Be	–29 to –30	Colorless	63	(4), 21
Cp ₂ Mg	176–178	Colorless	40	(1), 20, 22, 106, 107; (9), 36, 108
CpMgBr	—	Colorless	—	(2), 109, 118, 119
MeCp ₂ Mg	29–30	Colorless	45	(9), 107, 111
Cp ₂ Ca	dec without melting	Colorless	17	(1), 112; (2), 11, 112, 113
Cp ₂ Sr	dec without melting	Colorless	4.1	(1), 112; (2), 112
Cp ₂ Ba	dec without melting	Colorless	0.2	(2), 112

Scandium Group and the Rare Earths

Cp ₃ Sc	240	Straw	75	(4), 114
Cp ₃ Y	295	Pale yellow	85	(4), 114
Cp ₃ La	395 (dec)	Colorless	25	(4), 114
MeCp ₃ La	155–156	Colorless	27	(4), 111
Cp ₃ Ce	435	Orange-yellow	72	(4), 114
Cp ₃ Pr	415	Pale green	83	(4), 114
Cp ₃ Nd	380	Reddish-blue	78	(4), 114
MeCp ₃ Nd	165	Reddish-blue	70	(4), 47
Cp ₃ Sm	365	Orange	75	(4), 114
Cp ₂ SmCl	dec 200	Yellow	50–60	(4), 116
CpSmCl ₂ ·(C ₄ H ₈ O) ₃	dec 50–240	Beige	30–60	(4, 11), 115
CpEuCl ₂	dec 50–240	Purple	30–60	(4, 11), 116
Cp ₃ Gd	350	Yellow	84	(4), 114
Cp ₂ GdCl	dec 140	Colorless	50–60	(4, 11), 116
CpGdCl ₂ ·(C ₄ H ₈ O) ₃	82–86 (dec)	Lavender	30–60	(4, 11), 115
MeCp ₃ GdCl	188–197	Colorless	50–60	(4, 11), 116
MeCp ₃ GdOOCCH ₃	207–209	Colorless	65	(11), 116
Cp ₃ Dy	302	Yellow	85	(4), 114
Cp ₂ DyCl	343–346 (dec)	Yellow	50–60	(4, 11), 116
Cp ₂ DyOCH ₃	dec > 235	Yellow	85	(4), 116
CpDyCl ₂ ·(C ₄ H ₈ O) ₃	85–90 (dec)	Colorless	30–60	(4, 11), 115
Cp ₂ HoCl	340–343 (dec)	Yellow-orange	50–60	(4, 11), 116
CpHoCl ₂ ·(C ₄ H ₈ O) ₃	84–92	Yellow	30–60	(4, 11), 115
Cp ₃ Er	285	Pink	88	(4), 114
Cp ₂ ErCl	dec > 200	Pink	50–60	(4, 11), 116
Cp ₂ ErOOCCH ₃	331–335 (dec)	Pink	45	(11), 116
Cp ₂ ErOOCH ₃	dec > 270	Pink	27	(11), 116
Cp ₂ ErOCH ₃	236–240	Pink	52	(11), 116
Cp ₂ ErNH ₂	330–334	Pink	33	(11), 116
CpErCl ₂ ·(C ₄ H ₈ O) ₃	91–94	Pink	30–60	(4, 11), 115

TABLE I—continued

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
MeCp ₂ ErCl	119–122	Pink	50–60	(4, 11), 116
MeCp ₂ ErOOCCH ₃	199–201	Pink	55	(11), 116
Cp ₃ Yb	273	Dark green	82	(4), 114
Cp ₂ YbCl	dec > 240	Orange-red	50–60	(4, 11), 116
Cp ₂ YbOOCCH ₃	325–329 (dec)	Orange	65	(11), 116
Cp ₂ YbOOC ₆ H ₅	350–375 (dec)	Orange	54	(11), 116
Cp ₂ YbOCH ₃	290–305	Orange	60	(11), 116
Cp ₂ YbOC ₆ H ₅	382–386	Red	64	(11), 116
CpYbCl ₂ ·(C ₄ H ₈ O) ₃	78–81	Orange	30–60	(4, 11), 115
Cp ₂ LuCl	318–320	Greenish-white	72	(4, 11), 116
CpLuCl ₂ ·(C ₄ H ₈ O) ₃	76–78	Colorless	30–60	(4, 11), 115
<i>Thorium and the Actinides</i>				
Cp ₄ Th	dec 170	Colorless	1–40.7	(4), 57, 117
Cp ₄ U	dec 270	Red	6	(4), 14
Cp ₃ UCl	—	—	82–85	(4), 117
<i>Titanium Group</i>				
Cp ₂ Ti	dec 130	Green	40	(4), 120; (8), 121
Cp ₂ Ti·OC ₄ H ₉	81	Brown and green forms	—	(4), 120
Cp ₃ Ti	dec 130	Green	—	(4), 122
Cp ₄ Ti	—	Brown	—	(4), 421
Cp ₂ TiF ₂	—	Yellow	—	(11), 13
Cp ₂ TiCl ₂	287–287.5 (dec)	Red	72–90	(4), 13, 123–125; (5), 126; (2), 33

Cp_2TiBr_2	309–310 (dec)	Red	70	(4, 5), 13, 126, 127
Cp_2TiI_2	317–318	Purple	—	(11, 5), 13, 126
$\text{Cp}_2\text{Ti}(\text{OH})\text{Br} \cdot \text{H}_2\text{O}$	—	Orange	—	(11), 13
$\text{Cp}_2\text{Ti}(\text{Me})_2$	—	Orange	95	(11), 121, 186
$\text{Cp}_2\text{Ti}(\text{Me})\text{Cl}$	168–170 (dec)	Orange-red	95	(11), 121
$\text{Cp}_2\text{Ti}(\text{Et})\text{Cl}$	—	—	60	(11), 128
$\text{Cp}_2\text{Ti}\phi_2$ and other substituted derivatives	146–148	Orange-yellow	81	(11), 97, 129
$\text{Cp}_2\text{Ti}(\text{OEt})\text{Cl}$	91–92	Greenish-yellow	61	(4), 130, 131
$\text{Cp}_2\text{Ti}[\text{OSi}(\text{Me})_3]\text{Cl}$	1	Orange	—	(11), 350
$\text{Cp}_2\text{Ti}(\text{OSi}\phi_3)_2$	208–210	Yellow	—	(11), 350, 351
$\text{Cp}_2\text{Ti}(\text{S}\phi)_2$	200–201	Red	—	(11), 352
$\text{Cp}_2\text{TiCl}(\text{NH}_2) \cdot \text{NH}_3$	—	(Not fully identified)	—	(11), 132
$\text{Cp}_2\text{Ti}(\text{CH}_3\text{COO})_2$	126–128	Orange	93	(11), 202, 282, 289, 349
$\text{Cp}_2\text{TiCl}_2\text{Al}(\text{Et})_2$ and related compounds	126–130	Blue	—	(8), 121, 128, 135–139, 158, 159, 273
$[\text{Cp}_2\text{TiBr}]_2\text{O}$	—	—	—	(11), 140
$\text{Cp}_2\text{Ti}(\text{CO})_2$	90 (dec)	Red-brown	18	(11), 122, 133, 134
Cp_2TiCl	—	Green	68	(8), 13, 89, 121, 127, 137, 140, 141, 142
Cp_2TiBH_4	dec 150	Red-violet	83	(8), 154
CpTiCl_3	208–211	Yellow	84	(11), 95, 144–146, 149, 151; (5), 126
CpTiCl_2Br	165–170 (dec)	Orange	66	(11), 145
CpTiBr_3	174.5–175.5	Orange	25	(5), 126
CpTiI_3	184–186	Red	97	(5), 126
$(\text{CpTiCl}_2)_2\text{O}$	149–151	Yellow	91	(11), 144, 145, 148, 150, 152
$(\text{CpTiClO})_4$	285 (dec)	Yellow	—	(11), 150
$(\text{CpTiClO})_n$	—	—	78–92	(11), 145
$\text{CpTi}(\text{CH}_3)_3$	dec > 20	Yellow	77	(11), 121, 153
$\text{CpTi}(\text{OEt})_3$ and other alkoxy derivatives	(106–107/3)	Colorless	72	(4), 130, 131

TABLE I—continued

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Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
CpTi(OC ₄ H ₉) ₂ Cl	(145–150/2–3)	Colorless	80	(2), 160–162
CpTi(OR)Cl ₂ (R = alkyl)	—	—	—	(11), 145, 147
CpTi(OEt)(8-hydroxyquinolate) ₂	158–159	Yellow	—	(11), 296, 367
CpTiCl ₂	—	Blue	—	(8), 143
Cp(MeCp)TiCl ₂	—	—	—	(4), 145; (12), 393
(MeCp) ₂ TiCl ₂	217–218 (dec)	Red	26	(4), 47
MeCpTi(OC ₄ H ₉) ₂ Cl	—	—	60	(2), 162
C ₅ (CH ₃) ₅ TiCl ₃	—	Red-orange	20–30	(7), 81
Cp ₂ ZrCl ₂	244	Colorless	71–75	(4), 97, 155
Cp ₂ ZrBr ₂	260	Colorless	30	(5), 13, 127
Cp(C ₅ H ₄)ZrCl	~300	Colorless	—	(11), 156
Cp(C ₅ H ₄ SO ₃ H)ZrOSO ₃ H·(CH ₃ CO) ₂ O	—	—	—	(12), 97
CpZrCl ₃	—	—	—	(5), 157
CpZrCl(acetylacetonate) ₂	188–190	—	95	(11), 290
CpZr(CH ₃ COO) ₃	dec 170	—	65.7	(11), 367
CpZr(CH ₃ COO)(acetylacetonate) ₂	dec 128.5–131	—	70	(11), 367
(MeCp) ₂ ZrCl ₂	180–181	Colorless	38	(4), 47
Cp ₂ HfCl ₂	236	—	—	(4), 423
<i>Vanadium Group</i>				
Cp ₂ V	167–168	Violet	47–80	(4), 36, 164; (5), 119, 165; (8), 89; (2), 163
Cp ₂ VCl ₂ (also dibromide)	dec 250	Green	65	(4), 13, 27, 422; (5) 13, 127

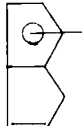
Cp_2VCl (also Br, I)	206–207	Blue	23.4	(4), 166; (8), 167
$\text{Cp}_2\text{V}\phi$	92	Black	50	(11), 168
$\text{Cp}_2\text{V}(\text{CH}_2\phi)$ and related phenyl-substituted derivatives)	109	Green	—	(12), 167
CpVCl_3 (also tribromide)	—	Dark green	42	(8), 166
CpVOCl_2 (also dibromide)	—	—	73–75	(8, 11), 166, 169
$\text{CpV}(\text{CO})_4$	138 (dec)	Orange	15–97	(11), 164, 170; (5), 119
$\text{K}_2[\text{CpV}(\text{CO})_3]$ (also Rb and Cs salts)	—	Yellow	68	(8), 164
$\text{CpV}(\text{CO})_2(\text{C}_4\text{H}_6)$	135–140 (dec)	Red	—	(11), 172
$\text{CpV}(\text{CO})_2(\text{C}_4\text{H}_{10})$	135–136 (dec)	Red	—	(11), 172
$\text{CpV}(\text{CO})_2(\text{C}_6\text{H}_8)$	98–100	Red	—	(11), 172
CpVC_7H_7	dec 130	—	—	(11), 171
$[\text{CpV}(\text{CH}_3\text{S})_2]_2$	dec 200	Brown-black	59	(11), 353
$[\text{CpV}(\text{CF}_3\text{SC}=\text{CSCF}_3)]_2$	Subl. 160/0.1	Green	50	(11), 354
Cp_4Nb	—	Blue	9.3	(4), 55
Cp_2NbCl_3	—	Brown	—	(4), 173
Cp_2NbBr_3	dec 260	Brown	70	(4), 13
$\text{Cp}_2\text{Nb}(\text{OH})\text{Cl}_2$	—	Yellow	—	(11), 173
$\text{Cp}_2\text{Nb}(\text{OH})\text{Br}_2$	—	Orange-red	—	(11), 13
$\text{Cp}_2\text{Nb}(\text{Cl})\text{BH}_4$	—	Red-violet	—	(8), 80
$\text{CpNb}(\text{CO})_4$	Subl. 60/0.1	Orange	2–3	(4, 11), 80
Cp_2TaCl_3	—	—	—	(4), 174
Cp_2TaBr_3	280 (dec)	Rust	9.3–62	(4), 13, 55; (5), 13
CpTaH_2	187–189 (dec)	Colorless	60	(4,8), 58, 175
<i>Chromium Group</i>				
Cp_2Cr	173	Scarlet	70–80	(4), 7, 12, 36, 176; (3), 43; (5), 45, 119
Cp_2CrI	dec 150	Green	100	(8), 177, 355
$[\text{Cp}_2\text{Cr}][\text{CpCr}(\text{CO})_3]$	190–193 (dec)	Brown	—	(11), 45
$[\text{Cp}_2\text{Cr}][\text{CpCrCl}_3]$	—	—	—	(8), 358

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
CpCrX ₂ (X = Cl, Br, I)	—	Green or blue	—	(11), 358
CpCrC ₆ H ₆	227–229	Orange	—	(5), 178
CpCrC ₇ H ₇	230	Blue-green	—	(8, 3), 356, 357
CpCrC ₇ H ₆ CH ₃	78	Black	—	(12), 179
CpCrBr (acetylacetonate)	190 (dec)	Dark green	3	(5), 180, 189
[CpCr(CO) ₃] ₂	163–168 (dec)	Colorless	37	(4, 8), 170; (11), 44
CpCr(CO) ₃ H	dec 57–58	Yellow	45	(4), 45, 190
[CpCr(CO) ₃] ₂ Hg	—	Yellow	40	(11), 44, 170
[CpCr(CO) ₄] ₂ BF ₃	—	—	—	(11), 181
CpCrC ₅ H ₇ (CO) ₂	74–75	Yellow	3.8	(11), 46, 182
CpCr(CO) ₂ NO	67–68	Orange-red	80	(11), 183, 184
CpCr(NO) ₂ X (X = F, Cl, Br, I, SCN, CN)	—	—	—	(11), 185
CpCr(NO) ₂ R (R = CH ₃ , CH ₂ Cl, C ₅ H ₅ , C ₂ H ₅ , C ₆ H ₅)	—	—	—	(11), 186, 187
[CpCr(NO) ₂ CO]PF ₆	—	Olive	45	(11), 187
CpCr(CH ₃ S) ₃ CrCp	(Subl. 180/0.2)	Purple	32	(11), 354
[CpCrO] ₄	74	Blue-violet	50	(8), 188
Cp ₄ Mo	dec > 220	Red-violet	39	(4), 191
Cp ₂ MoH ₂	183–185	Yellow	50	(4, 8), 56, 58, 190; (11), 192
Cp ₂ MoCl ₂	—	—	—	(4), 12
[Cp ₂ MoCl ₂] ₂ PtCl ₆	—	—	—	(8), 12
[CpMo(CO) ₃] ₂	(Subl. 150/0.1)	Red-violet	30	(3), 43; (8), 193; (4, 8), 170
CpMo(CO) ₃ H	(Subl. 50/0.1)	Yellow	50–52	(4), 170; (12), 44, 58
CpMo(CO) ₃ X (X = Cl, Br, I)	—	—	—	(11), 186

CpMo(CO) ₃ R (R = Me, Et, <i>i</i> -Pr)	—	—	78–85	(11), 186, 193
CpMo(CO) ₃ CF ₂ CF ₂ H	53–54	Orange-yellow	11	(11), 269, 362
CpMo(CO) ₃ (σ-CH ₂ CH=CH ₂)	dec 60	Yellow	40	(11), 361
[CpMo(CO) ₃ C ₂ H ₄]PF ₆	dec 104	Yellow soln.	24	(11), 360, 361
[CpMo(CO) ₄]PF ₆	—	—	—	(11), 363
CpMo(CO) ₂ C ₇ H ₇	230	Blue-green	—	(3), 356, 357
CpMo(CO) ₂ (π-allyl)	134 (dec)	Yellow	3	(UV light) 361
[CpMo(CO)C ₆ H ₆] ⁺	—	Red	19.1	(11), 364
[CpMo(CO) ₂ CH ₃ S] ₂	130 (dec)	Black	95	(11), 362
[CpMo(CH ₃ S) ₂] ₂	(Subl. 170–85/0.1)	Brown	54	(11), 354
CpMoO ₂ Cl	—	Yellow	3	(11), 361
[MeCpMo(CO) ₃] ₂	146–147	—	4.2	(4, 7), 47
[RC ₅ H ₄ Mo(CO) ₃] ₂ (R = alkyl)	—	Red or brown	20–70	(3), 51, 52
RC ₅ H ₄ Mo(CO) ₃ R' (R and R' are alkyl radicals)	—	—	—	(11), 51
φ ₃ P-C ₅ H ₄ Mo(CO) ₃	—	Yellow	60	(11), 359
[FluorMo(CO) ₃] ₂	195–197 (dec)	—	10	(3), 50
Azulene[Mo(CO) ₃] ₂	dec 150	Black	1	(3), 194
Cp(CO) ₃ Mo-W(CO) ₃ Cp	—	—	—	(11) 51
[Cp ₂ W] ₂ PtCl ₆	—	—	—	(4), 12
Cp ₂ WH ₂	163–165	Yellow	—	(4, 7), 56, 58, 190; (11), 192
Cp ₂ WH ₂ ·HCl	—	—	—	(12), 56
[CpW(CO) ₃] ₂	—	—	30	(3), 43
CpW(CO) ₃ H	—	—	65.5–67	(11), 44, 45
CpW(CO) ₃ Me	140 (dec)	Orange-red	80	(11), 45, 186
CpW(CO) ₃ Et	—	Orange-red	75	(11), 186
CpW(CO) ₃ CF ₂ CF ₂ H	65–65.5	—	8	(11), 362
[CpW(CO) ₃ C ₂ H ₄]PF ₆	dec 120	Yellow soln.	20	(11), 360
CpW(CO) ₂ NO	105–107	Orange-red	—	(11), 183, 186
[CpW(CO) ₂ CH ₃ S] ₂	dec 187	Dark red	63	(11), 362
[CpW(CO)(C ₆ H ₆)] ⁺	—	—	6.6	(11), 364

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
<i>Manganese Group</i>				
Cp ₂ Mn	172–173	Brown	45–75	(4), 36, 108, 196–198; (5), 203, 204
CpMn(CO) ₃	76.8–77.1	Yellow	40–80	(6, 11), 74–76, 108, 157, 241, 404–408, 410–419
CpMn(CO) ₂ C ₂ H ₄	116–118 (dec)	Orange-red	—	(11), 365
CpMn(CO) ₂ (1,3-cyclohexadiene)	80–81	Brown-yellow	—	(11), 366
[CpMn(CO) ₂] ₂ (1,3-cyclohexadiene)	dec 120	Yellow	19	(11), 366
[CpMn(CO) ₂ NO] ₂ PtCl ₆	dec 165–175	—	30	(11), 74
CpMn(CO) ₂ NC ₅ H ₅	114	Yellow-brown	53	(11), 205
CpMn(CO) ₂ Pφ ₃	216–218	Yellow	25	(11), 368
CpMn(CO) ₂ (CF ₃ C≡CCF ₃)	68	Orange	50	(11), 367
CpMn(π-diphenyl)	73–75	—	—	(4), 195
Cp ₃ Mn ₂ (NO) ₃	dec > 100	Purple-black	30	(11), 185
[CpMn(NO)S ₂] ₂	—	Brown-black	40	(11), 206
(MeCp) ₂ Mn	61–63	Brown	66	(4), 37, 47
MeCpMn(CO) ₃	70	Yellow	1.7–20	(6, 11), 47, 199–201, 409
MeCpMn(CO) ₂ NC ₅ H ₅	75	Yellow-brown	60	(11), 205
MeCpMn(CO) ₂ piperidine	—	Orange-red	—	(11), 369
 Mn(CO) ₃	—	—	40	(9), 82, 83, 208

FluorMn(CO) ₃	—	—	—	(11), 75
(1-COOH)(2-CH ₂ COOH)C ₅ H ₃ Mn(CO) ₃	—	—	—	(7) 82, 83
φ ₄ (OH)C ₅ Mn(CO) ₃	180 (dec)	—	53	(3), 49
[Cp ₂ Tc] ₂	155	Golden-yellow	—	(4), 209
CpTc(CO) ₃	—	—	—	(8), 143
Cp ₂ ReH	161–162	Yellow	20	(4), 60, 210
Cp ₂ ReH · HCl	—	Colorless	100	(12), 60, 210
CpRe(CO) ₃	111–114	Yellow	16	(3, 4, 11), 77, 211, 294
CpReC ₅ H ₆ (CO) ₂	111–112	Yellow	45–55	(11), 211, 212
CpReC ₅ H ₈ (CO) ₂	—	—	—	(12), 211
<i>Iron Group</i>				
Cp ₂ Fe	173–174	Orange	85–90	(4), 36, 174, 200, 217–219; (2), 18, 19, 33, 36, 38–40, 105, 125, 214–216, 224–229; (3), 42, 74; (1), 2, 213; (5), 42, 220, 221; (9) 48
[Cp ₂ Fe] ⁺	—	Purple soln.	—	(8), 86–88, 222, 223
Cp ₂ Fe ^{55,59}	—	—	—	(10), 230
[Cp ₂ FeH]AlCl ₃	—	—	—	(12), 348
CpFeFluor	74–76	Red-violet	0.5–8.8	(4, 5), 231, 232
CpFeC ₆ H ₇	—	—	—	(12), 233–235
CpFeC ₅ H ₄ C ₆ H ₅	109–110	Orange	—	(4), 68
CpFeC ₅ H ₄ CH ₂ C ₆ H ₅	76	—	—	(3), 48
CpFeC ₅ H ₃ (C ₆ H ₅) ₂	107	Orange	—	(3), 48
CpFeC ₅ H ₃ (CH ₃) ₂	—	Ivory	—	(11), 207
CpFeC ₅ H ₄ N=NR (R = Me, φ)	—	—	—	(4), 236
[CpFe(CO) ₂] ₂	194	Red-violet	194	(3), 12, 48, 74, 170, 237–241
CpFe(CO) ₂ H	— 5	Yellow	—	(11), 192
CpFe(CO) ₂ Cl	dec 87	Red	42–75	(8), 74, 242
CpFe(CO) ₂ Br	98–102 (dec)	Red-brown	65	(8), 48
CpFe(CO) ₂ I	119–120 (dec)	Black	65–72	(8), 170, 185; (11), 48

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (° C)	Color	Yield (%)	Methods of synthesis and references ^a
CpFe(CO) ₂ CN	dec 120	Yellow	46	(11), 74
[CpFe(CO) ₂] ₂ Hg	—	Gold-yellow	—	(11), 239
[CpFe(CO) ₂ C ₂ H ₄]PF ₆	dec 165	Yellow	60	(11), 344, 360, 370
CpFe(CO) ₂ Et	—	—	60	(11), 186, 344
CpFe(CO) ₂ (<i>σ</i> -Cp)	46	Red	15	(4), 243; (11), 187; (6), 48
CpFe(CO) ₂ φ	—	—	—	(11), 186
CpFe(CO) ₂ (C ₅ H ₄ C ₆ H ₅)	—	—	—	(6), 48
CpFe(CO) ₂ (CH ₂ CH=CH ₂) and related compounds	—	—	—	(11), 377, 379, 380
CpFe(CO) ₂ Si(CH ₃) ₃	70	Orange	42	(11), 345
CpFe(CO) ₂ (CF=CFCF ₃)	69.5–70.5	Orange	—	(11), 269, 346, 347
[CpFe(CO) ₂] ₂ R [R = (CH ₂) _n , CH ₂ C≡CCH ₂ , C ₃ N ₃ Cl]	—	Orange	—	(11), 383
CpFe(CO) ₂ RCO (R = alkyl)	—	—	14–63	(11), 371, 372
CpFe(CO) ₂ (C ₆ H ₅ COS)	125–126	Orange	26	(11), 371
[CpFe(CO)CH ₃ S] ₂	104–105	Brown-black	—	(11), 373
CpFe(CO)(I)(CNC ₆ H ₅)	89	Black	—	(11), 244
Cp(CO)Fe(CO) ₂ NiCp	132	Brown	—	(11), 245
Cp(CO) ₂ FeMo(CO) ₃ Cp	209	Red-violet	—	(11), 246
CpFe(CO) ₂ Mn(CO) ₅	76	Red	—	(11), 246
Cp(CO)Fe(CO) ₂ Co(CO) ₃	52–53	Red	—	(11), 382
CpFe(CO) ₂ Snφ ₃	139–141	Orange	39	(11), 378, 381
CpFe(CO) ₂ SnCl ₃	150 (dec)	Red-brown	85	(11), 381
CpFe(CO) ₂ Pφ ₃ Cl·3H ₂ O	—	Yellow	—	(11), 374
[CpFe(CO) ₃] ⁺	3	Yellow soln.	37–100	(11), 360, 374–376

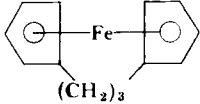
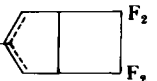
(CpFeC ₆ H ₆)Bφ ₄	dec 250–251	Yellow	60	(11), 297
(MeCp) ₂ Fe	37–39	Orange	65	(4), 47; (3), 47
(φCp) ₂ Fe	154	Orange	—	(4), 68
(1,3-φ ₂ C ₅ H ₃) ₂ Fe	220–222	Orange	—	(5), 68; (3), 48
(1,2,4-φ ₃ C ₅ H ₂) ₂ Fe	227–228	Orange	—	(4), 68
(φ ₄ C ₅ H) ₂ Fe	322	Red	21 based on C ₅ H ₆	(4), 88
(φCH ₂ C ₅ H ₄) ₂ Fe	102	—	—	(4), 48
(φ ₂ CHC ₅ H ₄) ₂ Fe	162–163	Yellow	—	(4), 62, 68, 248
(φ ₃ CC ₅ H ₄) ₂ Fe	174–175	Orange	—	(4), 62
(MeCHC ₅ H ₄) ₂ Fe	(91/0.025)	Orange-red	74	(4), 62, 247, 248
[(Me) ₂ (Et)CC ₅ H ₄] ₂ Fe	—	—	—	(5), 404
(Me ₃ CC ₅ H ₄) ₂ Fe	29–30	Orange	94	(4), 63, 110, 247, 248
[(Me) ₂ φCC ₅ H ₄] ₂ Fe	133.5–135	—	90	(4), 62, 63, 247, 248
(CH ₂ =CCH ₃ C ₅ H ₄) ₂ Fe	58–59	Orange-red	65	(4), 63, 247
(RC ₅ H ₄) ₂ Fe (R = carbocyclic radicals)	—	—	—	(4), 61, 247
 (CH ₂) ₃	106–107	Orange	2.5	(4), 249, 250
(and related compounds)				
[(RC ₆ H ₄ CH ₂) ₂ C ₅ H ₃] ₂ Fe (R = H, <i>o</i> -Cl, <i>p</i> -Cl, <i>p</i> -CH ₃ , <i>p</i> -F, <i>m</i> -Br, <i>p</i> -Br)	—	—	10–30	(4), 251
(RN=NC ₅ H ₄) ₂ Fe (R = COOCH ₃ , COOEt, COOCH ₂ C ₆ H ₅)	—	—	—	(4), 236
[(CH ₃ C ₅ H ₃ O [⊖]) ₂ Fe]Na ₂	—	—	—	(4), 65
(Ind) ₂ Fe	184–185	Violet-black	11	(5), 66, 280, 424
(Tetrahydroind) ₂ Fe	18.5–19	Orange	—	(12), 253
(RInd) ₂ Fe (R = Me, Et, allyl, butyl, φ, benzyl)	—	—	—	(4), 293, 298
Bis(3α,4-dihydroazulenyl)iron	68	Red	17	(4), 247

TABLE I—continued

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
[EtCpFe(CO) ₂] ₂	61–62	Purple	1.6	(3), 252
φCpFe(CO) ₂ Br	82	Red	83	(8), 48
φCpFe(CO) ₂ (σ-Cp)	—	Red oil	—	(6), 48
[IndFe(CO) ₂] ₂	—	—	20	(3), 252
[TetrahydroindFe(CO) ₂] ₂	—	—	39 on spiran	(3), 252
(CH ₃ SiC ₅ H ₄) ₂ Fe and related silyl and siloxoferrocenes)	—	—	50	(4), 254, 255, 425
Cp ₂ Ru	199–200	Pale yellow	43–52	(4), 256, 257; (5), 118
[CpRu(CO) ₂] ₂	dec 185	Orange-red	60	(6), 72
CpRu(CO) ₂ H	—	Colorless liquid	—	(11), 258
CpRu(CO) ₂ I	103–105	Orange	—	(11), 258
CpRu(CO) ₂ Me also Et	39–40	Colorless	—	(11), 258
(Ind) ₂ Ru	199	Orange	61	(5), 259
Cp ₂ Os	229–230	Colorless	22–23	(4), 256, 260
[Cp ₂ OsOH]PF ₆	185 (dec)	Red-brown	80	(8), 260
[CpOs(CO) ₂] ₂	198	Yellow	1.8	(6), 261
CpOs(CO) ₂ Br	120–121	Yellow	—	(8), 261
(Ind) ₂ Os	214	Yellow	2.3	(5), 69
<i>Cobalt Group</i>				
Cp ₂ Co	173–174	Purple	75–96	(4), 9, 36, 53; (3), 42; (2), 36, 63
[Cp ₂ Co] ⁺	—	Yellow soln.	75–100	(7), 9, 85, 228, 262, 263
CpCoC ₅ H ₅	98–99	Red	85	(12), 89, 90, 233
CpCoC ₅ H ₅ CH ₃	—	—	30	(12), 264
CpCoC ₅ H ₅ C ₆ H ₅	128–129	Red	80	(12), 349

CpCoC ₅ H ₅ COC ₆ H ₅	125.5–127	Red	80	(12), 349
CpCoC ₅ H ₅ CCl ₃	78–80	Orange-red	45	(12), 264, 265
CpCoC ₅ H ₅ CHCl ₂	—	—	—	(11), 264
CpCoC ₅ H ₅ CF ₃	—10	Red	—	(12), 264, 384
CpCoC ₅ H ₅ CF ₂ CF ₂ C ₅ H ₅ CoCp	dec 140	Red-brown	—	(12), 384, 385
CpCoC ₅ H ₅ C ₅ H ₄ C ₅ H ₅ CoCp	dec 100	Red	90	(12), 266
CpCo(1,3-cyclohexadiene) and related compounds	—	—	—	(11), 394, 395
CpCo[tetra(trifluoromethyl)cyclobutadiene]	264	Orange-yellow	—	(11), 396, 397
CpCo(tetraphenylcyclobutadiene)	—	—	—	(11), 396, 397
CpCo(π -R) (R = C ₈ H ₈ , C ₈ H ₁₂ , ϕ C \equiv C ϕ)	—	—	—	(11), 390–392
(CpCoC ₆ H ₆)(PF ₆) ₂	—	Yellow	40	(11), 386
CpCo(CO) ₂	—22	Red	80	(3), 74; (11), 170, 267, 268
CpCo(CO)CF ₃ I	dec 145	Black	1	(11), 394
CpCo(CO)(C ₂ F ₅)I	138	Black	—	(11), 394
CpCo(CO)(C ₃ F ₇)I	120	Black	—	(11), 269, 270
CpCo(CO)(CF ₂ CF ₂ CF ₂ CF ₂)	106–107	Pale yellow	—	(11), 388
[CpCoC ₃ H ₄ (CO)]PF ₆	dec 110	Green-yellow	36	(11), 389
[CpCo(CH ₃ S)] ₂	—	Black	—	(11), 373
CpCoCF ₃ SC=CSCF ₃	150	Violet	76	(11), 354
CpCo(tetramethylcyclopentadienone)	—	—	—	(7), 387
MeCpCoC ₅ H ₅ Me	—	—	—	(11), 264
MeCpCo(CO) ₂	—	Red	65	(11), 267
(Ind) ₂ Co	178–181	Black	—	(4, 5), 271
[(Ind) ₂ Co] ⁺	—	Yellow	—	(5), 271, 272
[(C ₅ H ₅ COOH) ₂ CO]Br	—	—	—	(8), 349
[(CH ₃ C ₅ H ₃ OH) ₂ Co]Cr(NH ₃) ₂ (SCN) ₄	154–157	Orange-brown	—	(4), 65
Cp ₂ Rh ¹⁰⁵	—	—	—	(10), 273
Cp ₂ RhX (X = Cl ⁻ , OH ⁻ , Br ₃ ⁻ , [Cr(CNS) ₄ NH ₃] ⁻)	—	—	—	(5), 274
CpRhC ₅ H ₆	118–120	Orange-yellow	26.8	(6), 275, 276

TABLE I—continued

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
CpRh(C ₂ H ₄) ₂	72–73	Yellow	47	(4), 277
CpRh(1,5-cyclooctadiene)	108–108.5	Yellow	—	(4), 278, 279
CpRh(cyclooctatetraene)	106	Yellow	11	(11), 280
[CpRh(CO) ₂] ₂	–11	Orange	26.8	(6), 71; (8), 398
(Cp ₂ Ir)Cr(CNS) ₄ NH ₃	—	—	—	(5), 274
CpIrC ₅ H ₆	130–132	Yellow	1	(4), 275
CpIr(CO) ₂	—	Yellow liquid	95	(6), 70
<i>Nickel Group</i>				
Cp ₂ Ni	173–174 (dec)	Green	42–96	(4), 8, 15, 53, 217, 281, 283; (2), 34, 36, 125, 163; (3), 42, 284
(Cp ₂ Ni) ⁺	—	Yellow soln.	—	(8), 8, 127, 142
CpNiC ₃ H ₇	73–75	Red-violet	30	(4), 285, 304
CpNiC ₅ H ₇	41–42	Red	18	(3), 286, 302, 305, 306
CpNiNO	(49/27)	Red	45–90	(3, 11), 74, 183, 299–301
(CpNiCO) ₂	146–147 (dec)	Green	50–74	(11), 287, 288, 307, 309
Cp ₃ Ni ₃ (CO) ₂	dec 200	Dark green	40.5–82	(11), 288, 307, 309, 311
CpNi(CO)I	dec 20	Violet	28	(8), 309
(CpNi) ₂ C ₂ H ₂	143–144	Green	48	(11), 303, 307, 310, 396, 399
and related compounds of substituted acetylenes				
CpNi[2,3-bis(methoxycarbonyl)-2π,5- norbornadien-7-yl]	84	Red	—	(12), 400
CpNi- 	93–94	Red	5.7	(12), 401

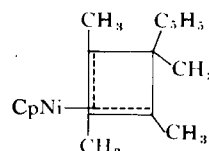
$\text{CpNiC}_5\text{H}_4\text{N}=\text{NC}_6\text{H}_5$	118–119	Purple	—	(11), 402
$[\text{CpNi}(\text{CNC}_6\text{H}_5)]_2$	91	Red	—	(11), 244
$\text{CpNi}(\text{P}\phi_3)\text{Cl}$	dec 140	Red	—	(11), 420
	—	—	—	(4), 277, 308
$(\text{MeCp})_2\text{Ni}$	39–40 (dec)	Green	36	(4), 47
$\text{MeCpNiC}_5\text{H}_6\text{CH}_3$	(30–35/0.1)	Red oil	11	(3), 312
$(\text{Ind})_2\text{Ni}$	—	Red-brown	—	(4), 271
$[\text{CpPdCl}]_2$	—	Red	100	(2), 313
CpPdC_3H_5	63–64	Red	—	(4), 304, 306, 314
CpPdC_6H_9	69	Red	60	(4), 306, 315
CpPdC_7H_7	dec 25	Red-violet	26	(4), 312
$\text{CpPdC}_{10}\text{H}_{12}\text{OCH}_3$	(Subl. 80/1)	Orange	40	(4), 277
$\text{CpPd}-\pi-[(\text{CH}_3)_2\text{CCHCHC}(\text{CH}_3)_2\text{OCH}_3]$	57–58	Red	—	(4), 403
$\text{RCpPdC}_3\text{H}_5$ (R = CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, C_3H_5)	—	—	—	(4), 314
$\text{MeCpPdC}_6\text{H}_9$	1–3	Red	37	(4), 312, 315
$\text{CpPt}(\text{CH}_3)_3$	65	Colorless	—	(4), 316
$(\text{CpPtCO})_2$	103 (dec)	Red	58	(4), 73
$\text{CpPt}(\text{CO})\text{I}$	55 (dec)	Black	45	(11), 73
<i>Copper Group</i>				
$\text{CpCu} \cdot \text{P}(\text{Et})_3$	127–128	Colorless	60	(2), 32, 317
<i>Zinc Group</i>				
Cp_2Zn	dec 100–130	Colorless	14–60	(4), 54, 318, 319
Cp_4Zn	—	—	41	(5), 320
CpZnEt	69–70	Colorless	33–50	(5), 321, 322
$\text{CpZn}\phi$	74–76	Colorless	9–50	(5), 322

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references ^a
CpZn(<i>t</i> -butyl)	—	Colorless	8	(5), 322
CpZnCl	—	Colorless	—	(5), 323
Cp ₂ Hg	83–85 (dec)	Yellow	20	(4), 32; (2), 224
CpHgCl	—	—	—	(2), 224
IndHgBr	118	—	9	(4), 324
<i>Boron Group</i>				
Cp ₃ B	138–139	Colorless	—	(4), 324; (5), 290
CpBF ₂	38–41	Colorless	—	(5), 290
Cp ₃ Al	50–60	Gray	95.6	(From Cp ₂ Hg), 325, 326
CpAl(Et) ₂	(47.5/0.005)	—	61.5	(4), 327
Na[CpAl(Et) ₃]	—	—	—	(4), 328
CpIn	dec 110	Pale yellow	55–65	(4), 329, 330; (1), 21
Cp ₃ In	dec 130	Golden yellow	—	(4), 329
MeCp ₃ In	60 (dec)	Yellow	—	(1), 21
CpTl	dec 230	Colorless	61–95	(2), 27, 29, 331, 332
MeCpTl	88–89	Yellow	76	(2), 47, 333; (1), 21
<i>Silicon Group</i>				
CpSi(Me) ₃	(73/25)	Colorless	40–45	(5), 334; (4), 32, 291
CpSiCl ₃	(52–55/10)	Colorless	40	(4), 335, 336; (2), 292
FluorSi(Me) ₂	178–179	Colorless	—	(4), 337
FluorSi(Me) ₃	97.5	Colorless	—	(4), 337
[FluorSi(Me) ₂] ₂ O	216–217	Colorless	—	(4), 337
C ₁₃ H ₈ [Si(Me) ₃] ₂	110	Colorless	—	(2), 337
CpGeCl ₃	(76/10)	Colorless	—	(2), 295
CpGe(Me) ₃	(32/9)	Colorless	62	(11), 295
CpGe(Et) ₃	(105/16)	Colorless	—	(5), 295, 338
Ce(CpC ₄ H ₉) ₃	(109/0.4)	Colorless	—	(5), 338

CpGe ϕ_3	176–177	Colorless	—	(5), 338
Ind ₄ Ge	196–198	Colorless	—	(5), 338
Ind ₂ Ge(ϕ) ₂	144–145	Colorless	—	(5), 338
IndGe(Et) ₃	(161/4)	Colorless	—	(5), 338
IndGe(ϕ) ₃	126	Colorless	—	(5), 338
FluorGe(Et) ₃	(165/0.5)	Colorless	—	(5), 338
FluorGe(ϕ) ₃	214	Colorless	—	(5), 338
Cp ₂ Sn	104–105	Colorless	50–60	(4), 54
Cp ₄ Sn	71–73	Yellow	41.5	(5), 320
Cp ₃ Sn ϕ	64–65	Yellow	40	(5), 320
Cp ₂ Sn(ϕ) ₂	105–106	Yellow	70	(5), 320
Ind ₄ Sn	215	Colorless	48.4	(4), 339, 340
Ind ₂ Sn(ϕ) ₂	116–117	Colorless	40	(4), 339, 340; (5), 320
IndSn(ϕ) ₃	128	Colorless	68	(4), 339, 340; (5), 320
Fluor ₄ Sn	290 sinter dec 310	Colorless	41	(4), 339, 340
Fluor ₃ Sn ϕ	262 (dec)	Colorless	50	(4), 339, 340
Fluor ₂ Sn(ϕ) ₂	179	Colorless	60	(4), 339, 340
Fluor ₂ Sn(ϕ)Cl	143	Colorless	—	(11), 339, 340
FluorSn(ϕ) ₃	129–130	Colorless	67.7	(4), 339, 340
FluorSn(ϕ)Cl ₂	140–141	Colorless	—	(11), 339, 340
2-(Me) ₂ N-C ₁₃ H ₈ Sn(ϕ) ₃	151	Colorless	60	(4), 339, 340
Cp ₂ Pb	132–135	Yellow	25	(4), 15, 281, 341
IndPb(ϕ) ₃	122	—	75	(4), 324
FluorPb(ϕ) ₃	118–120	—	75	(4), 324
<i>Arsenic Group</i>				
CpAs	—	Black	—	(4), 342
CpSb	—	Red	50–60	(4), 342, 343
Cp ₄ Sb ₂	—	Red-violet	83	(4), 343
Cp ₃ Bi	dec 75	Red-orange (Black form, stable > 15°)	50–60	(4), 342, 343
MeCp ₃ Bi	—	—	68	(4), 343

^a Roman numbers in parentheses indicate Method; italic numbers indicate references.

Melting points are given for solids. For liquids the boiling point and pressure of measurement are enclosed in parentheses and are listed in the melting point column. When the compound melts with decomposition, (dec) is placed after the melting point. When the compound decomposes without melting, dec is placed before the decomposition point. The numbers enclosed in parentheses in the final column refer to methods of synthesis in the text.

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